434. *Volume of Mixing in Some Non-electrolyte Mixtures.*

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Volume of mixing has been determined for several binary mixtures of non-electrolytes. Excess volume of mixing is in qualitative agreement with Prigogine's cell-model theory. Inversion of sign occurs in the *cyclo*hexane–*cyclo*hexanol mixture which is predicted by the latest refined theory.

PRIGOGINE'S cell-model theory of solutions predicts the sign of the main excess thermodynamic functions and the relations between them by utilizing only the molecular data.[1] It does not give a quantitative picture in view of the basic assumptions involved. A more recent theory,[2] developed by Prigogine and his co-workers, combines the advantages of the cell-model theory and Longuet-Higgins's theory of conformal solutions.[3] It is an inherent advantage of the two theories that the experimentally simplest thermodynamic quantity, *viz.*, volume of mixing, can be compared against the predicted values. The object of the present paper is to test the theories for some more mixtures and get an idea about intermolecular forces in solution.

EXPERIMENTAL

The substances were purified by repeated distillation. Excess volume of mixing was determined from density measurements. Corrections were made for the effect of buoyancy of air and for the weight of the vapour in the pycnometer tubes. The density measurements at 30° are tabulated. Timmermans's values for pure components are given for comparison.[4b]

Mol. fract. of C_6H_6	d^{30}
Benzene–toluene	
0	0·8553
0·2176	0·8573
0·3739	0·8616
0·5577	0·8619
0·7045	0·8626
0·8812	0·8663
1	0·8679

Mol. fract. of C_6H_6	d^{30}
*Benzene–*p*-xylene*	
0	0·8530
0·1689	0·8544
0·2612	0·8552
0·3898	0·8567
0·4703	0·8575
0·5815	0·8590
0·6517	0·8590
0·7450	0·8621
0·8090	0·8633
0·8814	0·8651
0·9282	0·8663
1	0·8679

Mol. fract. of C_6H_6	d^{30}
*Benzene–*o*-xylene*	
0	0·8711
0·2422	0·8690
0·3517	0·8681
0·4410	0·8676
0·6127	0·8676
0·7330	0·8674
0·7425	0·8676
0·8250	0·8678
0·8868	0·8680
0·9394	0·8682
1	0·8679

Mol. fract. of C_6H_6	d^{30}
*Benzene–*m*-xylene*	
0	0·8560
0·1545	0·8565
0·2431	0·8570
0·3636	0·8577
0·4451	0·8587
0·4996	0·8593
0·6160	0·8609
0·6940	0·8622
0·7626	0·8634
0·8252	0·8647
0·9352	0·8669
1	0·8679

Mol. fract. of *p*-C_8H_{10}	d^{30}
o-*Xylene–*p*-xylene*	
0	0·8711
0·1148	0·8689
0·1979	0·8679
0·2659	0·8663
0·3557	0·8652
0·4385	0·8629
0·5332	0·8612
0·6950	0·8583
0·8485	0·8555
0·9094	0·8547
1	0·8530

Mol. fract. of MeOH	d^{30}
Water–methyl alcohol	
0·1052	0·9690
0·1832	0·9508
0·2768	0·9271
0·3609	0·9090
0·4682	0·8919
0·4729	0·8861
0·6575	0·8450
0·7133	0·8482
0·8469	0·8189
1	0·7822

Mol. fract. of $C_6H_{12}O$	d^{30}
cyclo*Hexane–*cyclo*hexanol*	
0	0·7705
0·0500	0·7780
0·1836	0·7988
0·3261	0·8238
0·3499	0·8284
0·4494	0·8472
0·5061	0·8581
0·5520	0·8652
0·6147	0·8786
0·6609	0·8884
0·8343	0·9203
1	0·9484

Timmermans gives : benzene 0·8523; toluene 0·8577; *p*-xylene 0·8684; *o*-xylene 0·8716; *m*-xylene 0·8555; methyl alcohol 0·7818; *cyclo*hexane 0·7693.

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[1] Prigogine and Mathot, *J. Chem. Phys.*, 1952, **20**, 49; Prigogine and Bellemans, *Discuss. Faraday Soc.*, 1953, **15**, 80; Mathot and Desmyter, *J. Chem. Phys.*, 1953, **21**, 782; Mathot, Staveley, Young, and Parsonage, *ibid.*, 1955, **23**, 1551..

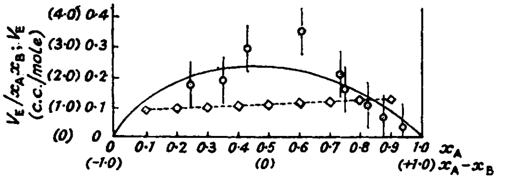
[2] Prigogine, Bellemans, and Englert-Chowles, *J. Chem. Phys.*, 1956, **24**, 518.

[3] Longuet-Higgins, *Proc. Roy. Soc.*, 1951, *A*, **205**, 247.

[4] (*a*) Partington, " An Advanced Treatise on Physical Chemistry," Longmans, London, 1949; (*b*) Timmermans, " Physical Constants of Pure Organic Compounds," Elsevier, Amsterdam, 1950; (*c*) Hirschfelder, Curtiss, and Bird, " Molecular Theory of Gases and Liquids," John Wiley and Sons, Inc., New York, 1954.

By using these values of densities, excess volumes V_E have been calculated and are plotted against mole-fractions for some cases in Figs. 1—4. The dotted curves are obtained when V_E/x_Ax_B is plotted against $(x_A - x_B)$. The following equations are found to fit the experimental curves.

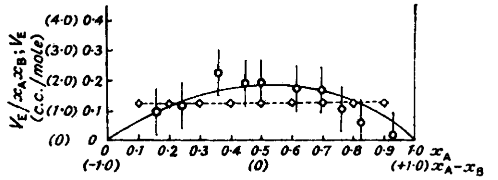
FIG. 1. *Volumes of mixing in benzene–*o*-xylene.*



———— V_E plotted against x_A.

- - - - V_E/x_Ax_B plotted against $x_A - x_B$.

FIG. 2. *Volume of mixing in benzene–*m*-xylene.*



———— V_E plotted against x_A.

- - - - V_E/x_Ax_B plotted against $x_A - x_B$.

(Figures in parentheses refer to the scale of the latter curve.)

FIG. 3. *Volume of mixing in methyl alcohol–water.*

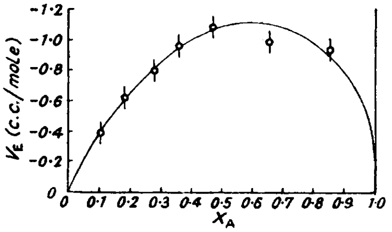
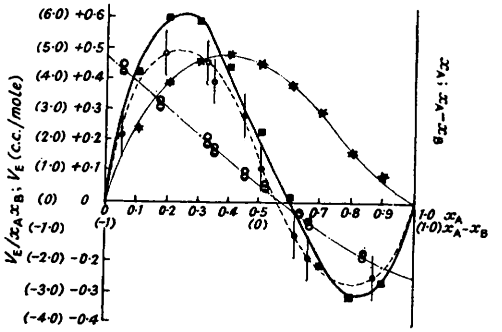


FIG. 4. *Volume of mixing in* cyclo*hexanol–*cyclo*hexane.*



ϕ *Experimental curve.*

✱ *Theoretical curve according to cell-model theory.*

■ *Theoretical curve according to latest refined theory.*

○ V_E/x_Ax_B, *plotted against* $x_A - x_B$ *according to proposed empirical equation.*

● V_E/x_Ax_B, *experimental.*

(Figures in parentheses refer to the plot of V_E/x_Ax_B against $x_A - x_B$.)

For *cyclo*hexane–*cyclo*hexanol:

$$V_E = x_Ax_B[0{\cdot}42 - 3{\cdot}6(x_A - x_B) + 0{\cdot}68(x_A - x_B)^2]$$

For benzene–*o*-xylene:

$$V_E = x_Ax_B[1{\cdot}12 + 0{\cdot}2(x_A - x_B) - 0{\cdot}1(x_A - x_B)^2]$$

For benzene–*p*-xylene:

$$V_E = 0 \text{ (slightly positive)}$$

For benzene–*m*-xylene:

$$V_E = x_Ax_B[0{\cdot}76 + 0{\cdot}03(x_A - x_B) - 0{\cdot}2(x_A - x_B)^2]$$

No fit was obtained for the water–methyl alcohol system. For the rest of the systems studied, the excess volumes of mixing are negligible within experimental error.

DISCUSSION

The essential assumptions underlying the original cell-model treatment by Prigogine *et al.* (1952) are the following: (1) The molecules of the constituents A and B are spherical in shape with isotropic fields of forces. (2) The distance of maximum interaction for AA, AB, and BB pairs is about the same (this assumption has been dispensed with in subsequent papers). (3) There is random mixing. (4) The mean potential field in the cage is of the smoothed potential type (vertical walls and flat bottom) with both depth and width depending on the concentration of the mixture. Assumption (4) has been dispensed with in the later treatment by Prigogine *et al.* (1956). In both treatments the potential is assumed to be 6–12 Lennard-Jones potential.

According to the original cell-model theory the excess volume of mixing is given by the expression :

$$\begin{aligned}\gamma V_{\mathrm{E}}/(\gamma_{\mathrm{AA}}{}^{*})^{3} = {} & 0{\cdot}9161\ [4{\cdot}125\rho^{2} + 0{\cdot}75\rho\delta + 1{\cdot}50\rho\delta(x_{\mathrm{A}} - x_{\mathrm{B}})]x_{\mathrm{A}}x_{\mathrm{B}} \\ & +2{\cdot}032\ \boldsymbol{k}T/\Lambda_{\mathrm{AA}}[-2\theta - 0{\cdot}75\delta^{2} + \theta\delta(1 + 2x_{\mathrm{B}}) + \theta^{2} - 10{\cdot}44\rho^{2} - 3\rho\delta \\ & - 2{\cdot}55\rho\theta(x_{\mathrm{A}} - x_{\mathrm{B}}) + 0{\cdot}227\rho\delta]x_{\mathrm{A}}x_{\mathrm{B}}] \quad . \quad . \quad . \quad . \quad . \quad (1)\end{aligned}$$

where γ is a geometrical factor depending on the lattice assumed, $\gamma_{\mathrm{AA}}{}^{*}$ is the radius of an A molecule in pure A, $\rho = (\gamma_{\mathrm{BB}}{}^{*} - \gamma_{\mathrm{AA}}{}^{*})/\gamma_{\mathrm{AA}}{}^{*}$ represents the difference in size of the A and B molecules, $\delta = (1/\Lambda_{\mathrm{AA}})[\Lambda_{\mathrm{BB}} - \Lambda]_{\mathrm{AA}}$,

and $$\theta = (1/\Lambda_{\mathrm{AA}})\left[\Lambda_{\mathrm{AB}} - \frac{\Lambda_{\mathrm{BB}} + \Lambda_{\mathrm{AA}}}{2}\right]$$

where $\Lambda_{\mathrm{ij}} = Z/\varepsilon_{\mathrm{ij}}{}^{*}$ where Z is the number of molecules which are nearest neighbours to any given molecule, and $\varepsilon_{\mathrm{ij}}{}^{*}$ represents the force constant of interaction between molecules i and j. x_{A} and x_{B} are the mole fractions of components A and B, $\boldsymbol{k}$ is Boltzmann's constant, and T is the absolute temperature.

According to the latest theory of Prigogine *et al.* the excess volume of mixing is given by the expression :

$$\begin{aligned}V_{\mathrm{E}}/x_{\mathrm{A}}x_{\mathrm{B}} = {} & \tfrac{3}{2}v_{\mathrm{AA}}\rho[\theta(x_{\mathrm{A}} - x_{\mathrm{B}}) + \tfrac{1}{2}\delta + \tfrac{11}{4}\rho] \\ & + Tv_{\mathrm{AA}}{}'[-2\theta - 9\rho^{2} + \theta^{2} - \tfrac{3}{4}\delta^{2} + \theta\delta(1 + 2x_{\mathrm{B}}) - 3\rho\theta + \tfrac{9}{4}\rho\delta + \tfrac{3}{2}\rho\theta(x_{\mathrm{A}} - x_{\mathrm{B}})] \\ & + \tfrac{1}{2}T^{2}v_{\mathrm{AA}}{}''[\theta^{2} - \tfrac{3}{4}\delta^{2} + \theta\delta(1 + 2x_{\mathrm{B}})] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)\end{aligned}$$

where ρ, θ, δ, x_{A}, x_{B}, and T have the same significance as before, v_{AA} is the molar volume of the pure component A used as a reference substance, and $v_{\mathrm{AA}}{}'$ and $v_{\mathrm{AA}}{}''$ represent first and second differentials with respect to T.

The excess volume has been calculated by using the above equations for our mixtures, except aqueous methyl alcohol. The values of the constants Λ and γ^{*} used in the calculation for various liquids (with *cyclo*hexane as the reference) are tabulated.

	Λ			γ *			
Substance	from T_{c}	from heat of vapn.	Mean	from V_{c}	from d	from η	Mean
*cyclo*Hexane	1·000	1·000	1·000	1·000	1·000	1·000	1·000
Benzene	1·014	1·015	1·015	0·940	0·939	0·865	0·915
Toluene	1·0715	1·0493	1·0604	1·0075	0·994	—	1·000
o-Xylene	—	1·1467	1·1467	—	1·0375	—	1·0375
m-Xylene	—	1·1317	1·1317	—	1·044	—	1·044
p-Xylene	—	1·1247	1·1247	—	1·044	—	1·044
*cyclo*Hexanol	—	0·583	0·583	—	0·983	—	0·983

From these values, δ and ρ have been calculated and the values are again tabulated along with the calculated and experimental excess volumes for $x_{\mathrm{A}} = x_{\mathrm{B}} = 0{\cdot}5$.

			Excess volume *			
System	δ	ρ	(obs.)	(calc.) eqn. (1)	(calc.) eqn. (2)	
Benzene–toluene	0·045	0·929	0	0·52	1·6	
	−0·043	−0·085		0·58	1·5	
Benzene–*m*-xylene	0·115	0·141	0·18	1·42	3·88	
Benzene–*o*-xylene	0·130	0·134	0·28	1·32	3·57	
	−0·115	−0·118		1·39	3·66	
Benzene–*p*-xylene	0·108	0·141	slightly	1·407	3·83	(30°)
	−0·098	−0·124	positive	1·502	3·70	
o-Xylene–*p*-xylene	−0·019	0·006	0	0	0	
*cyclo*Hexane–*cyclo*hexanol ...	−0·417	−0·017	—	—	—	

* The two values of excess volume for each system have been calculated by using each component as reference species respectively.

In the above calculations the values of v_{AA}, v_{AA}', and v_{AA}'' are determined from the tables given by Partington [7a] and from the values of densities at different temperatures.[7b]

The second Table indicates that for all the systems studied, the sign of the volume of mixing is predicted correctly by both the theories. Quantitative agreement is ruled out by the theories themselves in view of the restrictions imposed on the choice of the systems although the calculated excess volume by using both the equations agrees with the experimental value in the case of *o*-xylene–*p*-xylene system. Thus, benzene–*p*-xylene, etc., are not strictly spherical molecules and naturally exact quantitative agreement cannot be expected. That is probably why the values calculated by using equation (2) do not improve the agreement between theory and experiment.

Of the systems studied, *cyclo*hexane–*cyclo*hexanol mixtures conform most closely to the basic assumptions involved. *cyclo*Hexanol contains a hydroxyl group on account of which association can occur. Hence it affords a case when BB interactions are more prominent than AA or AB interactions. Obviously, this system offers a more stringent test of the theories. Accordingly we have compared the experimental volume of mixing curve with that calculated by using the two theories, in Fig. 5. In making the calculations we have used the relation, $\theta = -\delta/2$, on account of the predominance of BB interaction. It can be seen that the inversion of sign is not predicted by the cell-model theory for this system whereas the latest theory predicts it in agreement with experiment. Also the quantitative agreement is much better between theory and experiment for the latest theory.

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