Excess Volumes of Mixing

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The excess volumes of mixing for the following systems have been measured at 20 and 40° C: cyclohexane+t-butyl cyclohexane; cyclohexane+dicyclohexyl; cyclohexane+dicyclohexylmethane; cyclohexane+1,3-dicyclohexylpropane. The experimental measurements have been compared with the predictions of Prigogine's average potential, corresponding states theory of mixtures of molecules of different size.

It was hoped that the set of mixtures studied would correspond to the theoretical case of a common monomer, occupying one lattice site, mixed with a series of larger molecules each occupying approximately two lattice sites. One prediction of the Prigogine theory for such a theoretical situation is that, at constant composition and temperature, all the excess functions, including $v^{\rm E}$ and $dv^{\rm E}/dT$, will pass through a minimum as the size of the larger molecule is increased, the minimum occurring when the "dimer" occupies two lattice sites exactly. The experimental measurements confirm this prediction and are in reasonable qualitative agreement with the theory.

Prigogine has extended the average potential, corresponding states theory of liquid mixtures ¹⁻³ to include polymer solutions.⁴ There has been little attempt to test the predictions of the theory against the appropriate experimental properties of suitably chosen systems. The few tests which have been carried out ^{5, 6} suggest that the new theory is a considerable improvement on the older statistical treatments of the Flory-Huggins type based exclusively on a rigid lattice model.

If a common monomer is selected and mixed in turn with a series of polymer molecules of gradually increasing size, one prediction of the Prigogine treatment is that, at constant composition and temperature, all the thermodynamic excess functions should pass through a series of minima. These minima occur when the polymer molecule displaces an integral number of monomer molecules. This periodic behaviour should be particularly marked for the excess volume of mixing. The present paper describes an attempt to verify this prediction by measuring $v^{\rm E}$ and $dv^{\rm E}/dT$ for a series of monomer +" dimer " mixtures. The chosen monomer was cyclohexane which is non-polar and has a reasonably spherical force field and the " dimers ", in order of increasing molar volume, were t-butyl cyclohexane, dicyclohexyl, dicyclohexylmethane, 1,2-dicyclohexylethane, and 1,3-dicyclohexylpropane.

EXPERIMENTAL

DILATOMETRY

The excess volume of mixing was measured as a function of composition and temperature using a direct method. The apparatus was a slightly modified version of the dilatometer described by Desmyter and van der Waals.⁷ Using this type of instrument in which a known amount of one component is diluted with successive, known amounts of the second component, the excess volume of mixing can be obtained over the whole composition range at one temperature with only one filling of the dilatometer. It was a convenient apparatus to

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use because several of the dimers were only obtained in small amounts. The experimental volume changes were unexpectedly small, for equimolar mixtures v^{E} ranged from -0.17 cm³ mole⁻¹ to -0.016 cm³ mole⁻¹.

Full experimental details of the filling and operation of the dilatometer were given in the original publication and further information is available ⁸ concerning the additional precautions which had to be taken on account of the extremely small volume changes encountered in the present systems. After filling, the dilatometer was mounted in a large water thermostat of conventional design. The temperature control was $\pm 0.002^{\circ}$ C over a period of several hours. The absolute temperature was measured using mercury-in-glass thermometers which had been recently calibrated to $\pm 0.01^{\circ}$ C at the N.P.L. The heights of the various mercury levels in the dilatometer were measured to ± 0.01 mm using a cathetometer.

An analysis of experimental uncertainties led to the conclusion that the excess volume of mixing was measured to ± 0.003 cm³ mole⁻¹. The reproducibility of the results is shown in fig. 1, where runs A and B are duplicate experiments performed several weeks apart on the same system, cyclohexane+1,2-dicyclohexylethane at the same temperature, 20.00°C. The uncertainty in dv^{E}/dT was estimated to be ± 0.0005 cm³ mole⁻¹ deg.⁻¹



FIG. 1.—Reproducibility of measurements.

⊙, run A; ⊽, run B. The system is cyclohexane+1,2-dicyclohexylethane at 20.00°C.

MATERIALS

The measured physical properties of the substances used are given in table 1. The percentage purities were calculated from experimental freezing-point curves using the construction of Taylor and Rossini.⁹ Several of the dimers appeared to contain 2-3 % impurity

TABLE 1.—PHYSICAL	PROPERTIES	OF	COMPOUNDS
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substance	d_{4}^{20}	freezing point, °C	% purity
t-butyl cyclohexane	0.8110	-37.5	98
dicyclohexyl	0.8859	3.88	99.98
dicyclohexylmethane	0.8779	20.5	98·3
1,2-dicyclohexylethane	0.8772	+ 7.9	97.5
1,3-dicyclohexylpropane	0.8724	-15.4	97.8
cyclohexane	$0.7738 (d^{25})$	+ 5.55	99.7

but analysis with a Griffin and George V.P.C. apparatus gave single, sharp peaks for all compounds indicating that any impurity present was probably isomeric with the major component.

CYCLOHEXANE.—Hopkin and Williams Spectrosol grade material was purified by a combination of fractional distillation and fractional crystallization. About 11. of material with a freezing point of $+5.55^{\circ}$ C was obtained and this was used for most of the measurements. Several more fractional crystallizations gave a small amount of cyclohexane with a freezing point of $+6.54^{\circ}$ C in agreement with recent ^{10, 11} determinations. This material gave excess volumes of mixing identical, within experimental error, with the results obtained using the slightly impure (99.7 %) cyclohexane. Experimental measurements of excess volumes of mixing are usually little affected by small amounts of impurity.

DICYCLOHEXYL.—Commercial grade material was obtained from L. Light and Co. Ltd., and was purified in a similar manner to the cyclohexane. The measured physical properties are in agreement with the measurements of Mears *et al.*¹²

t-BUTYL CYCLOHEXANE, DICYCLOHEXYLMETHANE, 1,2-DICYCLOHEXYL-ETHANE, 1,3-DICYCLO-HEXYLPROPANE.—These substances were prepared by the hydrogenation of the corresponding aromatic compounds, which were first purified by distillation or crystallization. The hydrogenations were carried out in a small autoclave at a hydrogen pressure of 100 atm and a temperature of 220°C. The starting materials were dissolved in cyclohexane and the catalyst was Nicat catalyst manufactured by J. Crosfield and Co. Ltd. The propane proved particularly difficult to hydrogenate. After reaction the compounds were freed from all aromatic impurity by passage, in cyclohexane solution, down a column packed with silica gel. The cyclohexane was then distilled off and the substances purified by fractional distillation and crystallization.

RESULTS

Each of the five binary systems was studied over the whole concentration range at 20 and at 40° C; the cyclohexane+dicyclohexyl system was also studied at 30° C. The results are given in fig. 2-6. There is only one independent measurement of



⊙, 20°C; ⊡, 40°C.

an excess volume of mixing for any of these systems, a value, determined from density measurements of -0.03 ± 0.05 cm³ mole⁻¹ for an equimolar mixture of cyclohexane and dicyclohexyl.¹³ This is in agreement with the value of -0.037 ± 0.03 cm³ mole⁻¹ interpolated from the present results.



FIG. 3.—The system cyclohexane+dicyclohexyl. \odot 20°C; \triangle , 30°C; \Box , 40°C.







In order to calculate the interaction parameters δ and ρ which occur in the theoretical equations for the excess functions a knowledge of the molar volume of each substance as a function of temperature was required. The density of each pure



⊙, 20°C; ⊡, 40°C.

component was measured over the appropriate temperature range using a conventional Sprengel pyknometer and a thermostatted silicone oil bath which could operate up to 220°C. The results of these measurements are given in table 2.

10mm %C	substance					
temp., C	cyclohexane	t-butyl C.H.	D.C.H.	D.C.H.M.	1,2-D.C.H.E.	1,3-D.C.H.P.
25			188.46	206.52	222.40	239.87
30	109.39	174.79	189.22	207.36	223.25	
40	110.76	176.52	190.77	209.09	225.07	
50	112.19	178.01	192.34	210.83	226.90	
60	113.65		193·94	212.56	228.70	
70	115.14	180.79				
80	116.69		197.19	216.14	232.70	
100		186.84	200.64	219.82	236.00	254.66
120			204·10	223.66	240.39	258-85
130		193-29				
140			207.48	227.73	244.62	
144.1		196·58				264.44
160			211.57	231.93	248.68	268.26
180			215.71	236.48	253.46	273.22
200			220·27	241.55	258.68	278.30
211.5			222.86			
215.6						280.33

TABLE 2	Molar	VOLUMES	OF	THE	PURE	COMPONENTS	IN	cm ³
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DISCUSSION

The Prigogine treatment of a monomer+polymer mixture assumes that the monomer and each individual segment of the polymer obey the same theorem of corresponding states, both in the pure liquid state and in the mixture. In addition, the three types of molecular encounter which occur in the mixture should follow a Lennard-Jones 6: 12 potential with force constants ε_{11}^* , r_{11}^* , ε_{22}^* , r_{22}^* and ε_{12}^* , r_{12}^* .

The three interaction parameters which appear in the final equations for the excess functions are directly related to these force constants,

$$\delta = (\varepsilon_{22}^* - \varepsilon_{11}^*)/\varepsilon_{11}^*, \ \rho = (r_{22}^* - r_{11}^*)/r_{11}^*, \ \theta = [\varepsilon_{12}^* - (\varepsilon_{11}^* + \varepsilon_{22}^*)/2]/\varepsilon_{11}^*.$$

In the monomer + polymer mixture the average potentials acting on a monomer molecule and on a segment of a polymer molecule are $\langle \varepsilon_1^* \rangle$, $\langle r_1^* \rangle$ and $\langle \varepsilon_2^* \rangle$, $\langle r_2^* \rangle$ respectively. It can be shown that,¹⁴ neglecting all terms in δ , ρ or θ of order higher than the second power, †

$$\langle \varepsilon_1^* \rangle / \varepsilon_{11}^* = 1 + X_2(\theta + \delta/2 - 9\rho^2 X_1),$$
 (1)

$$\langle r_1^* \rangle / r_{11}^* = 1 + \frac{1}{2} \rho X_2 [1 + (\theta + \delta/2) X_1 + 17 \rho X_1/4],$$
 (2)

$$\langle \varepsilon_2^* \rangle / \varepsilon_{11}^* = 1 + \delta + X_1 (\theta - \delta/2 - 9\rho^2 X_2),$$
 (3)

$$\langle r_2^* \rangle / r_{11}^* = 1 + \rho - \frac{1}{2} \rho X_1 [1 + (\theta - \delta/2) X_2 - 17 \rho X_2/4],$$
 (4)

where X_1 and X_2 are "surface fractions" defined as

$$X_1 = q_1 x_1 / (q_1 x_1 + q_2 x_2)$$
 and $X_2 = q_2 x_2 / (q_1 x_1 + q_2 x_2)$. (5)

 x_1 , x_2 are the mole fractions of monomer and polymer and q is defined in terms of Z, the co-ordination number of the liquid and r, the degree of polymerization of the polymer.

$$qZ = rZ - 2r + 2. \tag{6}$$

In the present case where component 1 is a monomer, $q_1 = 1$.

The final, explicit expression for the molar excess volume of mixing of a polymer + monomer mixture derived from eqn. 17.7.1 of ref. (4) is

$$v^{\rm E} = v_1 \bigg[x_1 \bigg(\frac{\langle r_1^* \rangle^3}{r_{11}^{*3}} - 1 \bigg) + r x_2 \bigg(\frac{\langle r_2^* \rangle^3}{r_{11}^{*3}} - \frac{r_{22}^{*3}}{r_{11}^{*3}} \bigg] + T \frac{dv_1}{dT} \bigg[\bigg(x_1 \frac{\langle r_1^* \rangle^3}{r_{11}^{*3}} + r x_2 \frac{\langle r_2^* \rangle^3}{r_{11}^{*3}} \bigg) \bigg(\frac{\varepsilon_{11}^*}{\langle \varepsilon^* \rangle} \frac{\bar{c}}{\bar{q}} - 1 \bigg) - r x_2 \frac{r_{22}^{*3}}{r_{11}^{*3}} \bigg(\frac{\varepsilon_{11}^*}{\varepsilon_{22}^*} \frac{c_2}{q_2} - 1 \bigg) \bigg] + \frac{1}{2} T^2 \frac{d^2 v_1}{dT^2} \bigg[\bar{r} \bigg(\frac{\bar{c}}{\bar{q}} \frac{\varepsilon_{11}^*}{\langle \varepsilon^* \rangle} - 1 \bigg)^2 - r x_2 \bigg(\frac{c_2}{q_2} \frac{\varepsilon_{11}^*}{\varepsilon_{22}^*} - 1 \bigg)^2 \bigg],$$
(7)

where v_1 is the molar volume of a standard reference substance at temperature T. c_2 is a parameter related to the flexibility of the polymer molecule, $3c_2$ being the number of external degrees of freedom of a polymer segment in the liquid state,

$$\langle \varepsilon^* \rangle = X_1 \langle \varepsilon_1^* \rangle + X_2 \langle \varepsilon_2^* \rangle, \tag{8}$$

$$q = x_1 q_1 + x_2 q_2 = x_1 + x_2 q_2, \tag{9}$$

$$c = x_1 c_1 + x_2 c_2 = x_1 + x_2 c_2, \tag{10}$$

and

$$r = x_1 r_1 + x_2 r_2 = x_1 + x_2 r_2. \tag{11}$$

The theoretical expression for dv^{E}/dT can be derived from eqn. (7), a term in $d^{3}v_{1}/dT^{3}$ appearing. v^{E} and dv^{E}/dT as functions of composition are obtained in terms of the quantities δ , ρ , θ , Z, c_{2} , r_{2} and certain physical properties of the pure reference substance. In the case considered, a monomer+dimer system, $r_{2} = 2$, $c_{2} = 5/3$ and Z, the average co-ordination number of the liquid was chosen as 6, although this latter choice has little effect on the numerical values of the excess functions.

⁺ The four equations given below are eqn. 17.3.4 to 17.3.7 of ref. (14). There are two misprints in these equations in the original publication.

Cyclohexane was chosen as the reference substance and the experimental values of the molar volume and its various derivatives used in the calculation of the theoretical excess functions are given in table 3.

TABLE 3.—SELECTED PROPERTIES OF THE REFERENCE SUBSTANCE, CYCLOHEXANE ¹⁵

property	20°C	40°C
v_1	108.10	110.80
$T dv_1/dT$	38.22	43.84
$T^2 d^2 v_1 / dT^2$	34.8	55.1
$T^2 d^3 v_1 / dT^3 + 2T d^2 v_1 / dT^2$	0.91	1.12

For all five experimental systems, δ and ρ were obtained from the molar volume against temperature data of table 2 by a superposition technique similar to that described by Bellemans and Naar-Colin.¹⁶ The numerical values of δ obtained are dependent on the magnitude of Z chosen and in table 4 are given δ and ρ for the five systems with Z = 6. For four of these mixtures, δ is constant within eperimental error indicating that these systems are a particularly suitable series against which to test the various predictions of the Prigogine theory. The differences in the experimentally measured excess functions are due entirely to variations in the size of the "dimer" molecule and not to any change in the intermolecular attracton. The cyclohexane+t-butyl cyclohexane system gives a lower value of δ , prolably due to the presence of methyl groups which are absent in all the other molecules.

	TABLE 4.—EXPERIMENTAL	, values of δ and $ ho$	
	system	δ	ρ
cyclohexane+	-t-butyl cyclohexane	0.15	-0.060
**	dicyclohexyl	0.35	-0.019
"	dicyclohexylmethane	0.35	+0.012
,,	1,2-dicyclohexylethane	0.37	+0.039
,,	1,3-dicyclohexylpropane	0.38	+0.066
		± 0.02	± 0.002

The interaction parameter θ depends on the nature of the unlike, 1-2, iteractions and there is no easy way of measuring this quantity experimentally. In all the calculations the geometric mean combining rule was assumed and θ we approximated by $-\delta^2/8$. Values of $v^{\rm E}$ and $dv^{\rm E}/dT$ as functions of composition fom eqn. (7) were obtained using a Ferranti Sirius computer. The theoretical and experimental excess volumes of mixing for equimolar mixtures at 20 and 40°C as a function of ρ are given in fig. 7. In the theoretical calculations an average value of $\delta = 0.36$ was used. Reasonable qualitative agreement is obtained. Both the theoretical and the experimental curves pass through a minimum in the region of $\rho = 0$, i.e., when the "dimer" exactly displaces two monomer units from he quasi-lattice. The experimental value for 1,2-dicyclohexylethane at 20°C is aromalous and no reasonable explanation of this can be suggested.

The quantitative agreement between theory and experimen is poor. This is another example of the tendency for theories of the Prigogine type to over-emphasize the contribution of differing molecular size to the thermodynamic excess functions.¹⁷ Variation of the numerical values of Z or θ has little or noeffect on the general shape of the theoretical curves but simply moves them vertically up or down with respect to the origin of the v^{E} against ρ graph.

The theoretical and experimental curves for dv^{E}/dT as a function of ρ are given in fig. 8. The point representing the cyclohexane+1,2-dicyclohexylethane system is again anomalous; the numerical agreement between theory and experiment is

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poor, but the appearance of a minimum in the experimental curve and the general similarity in the shapes of the two curves is satisfactory.

The poor quantitative agreement between theory and experiment for both $v^{\mathbf{E}}$ and $dv^{\mathbf{E}}/dT$ appears to be a feature of most recent attempts to fit solution theories

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based on the theorem of corresponding states to the experimentally measured properties of mixtures of real molecules.¹⁸ Although the series of mixtures studied here obey the theorem of corresponding states to a high degree of precision, at least with respect to molar volume, it may be that the relatively large value of $\delta = 0.36$ is too great to permit closer numerical agreement to be obtained.



FIG. 7.—Theoretical and experimental comparison for v^{E} .

A, expt. curve at 20°C; B, expt. curve at 40°C; C, theor. curve at 20°C; D, theor. curve at 40°C. FIG. 8.—Theretical and experimental comparison for dv^E/dT . A, expt. curve; B, theor. curve.

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