

# The liquid–liquid critical behaviour of binary solutions for (*N*-methyl-2-pyrrolidone + cycloalkanes)

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The critical temperatures and the critical compositions have been measured for binary solutions of {*N*-methyl-2-pyrrolidone (NMP) + methylcyclohexane}, (NMP + cyclohexane), (NMP + cyclooctane), and (NMP + propylcyclopentane). The dependence of the critical volume fraction on the molar volume of cycloalkanes has been discussed. The coexistence curves of (*T*, *n*), (*T*, *x*), and (*T*, *φ*) (*n*, *x*, and *φ* are refractive index, mole fraction, and volume fraction, respectively) for {NMP + methylcyclohexane} have also been determined within 8 K from the critical temperature by measurements of refractive index and proper conversions of *n* to *x*, and *x* to *φ*. The critical exponents *β* deduced from the three types of coexistence curves are consistent with theoretical predictions. The results have been analysed to obtain the critical amplitudes and Wegner-correction terms when *β* is fixed at the theoretical value. The goodness of the order parameters has been discussed by comparisons of the fits of the diameters of coexistence curves with  $\tau^{1-\alpha}$  and  $\tau^{2\beta}$  ( $\tau = (T_c - T)/T_c$ , where *T<sub>c</sub>* is the critical temperature). The coexistence curves have been successfully described by a combination of the Wegner equation and the expression for the diameter.

Determinations of the critical compositions and the coexistence curves of binary liquid mixtures in the critical region are important ways of investigating the critical phenomena. The differences ( $\rho_2 - \rho_1$ ) of concentration variables of coexisting phases may be expressed by the Wegner expression:<sup>1</sup>

$$\rho_2 - \rho_1 = B\tau^\beta + B_1\tau^{\beta+\Delta} + \dots, \quad (1)$$

where  $\rho_1$  and  $\rho_2$  are the “density” variables in upper and lower coexisting phases, *β* is the critical exponent relating to coexistence curve, *B* and *B<sub>1</sub>* are critical amplitudes and are system dependent. In a region sufficiently close to the critical temperature, eqn. (1) becomes:

$$\rho_2 - \rho_1 = B\tau^\beta. \quad (2)$$

The diameter  $\rho_d$  of the coexistence curve may be expressed by:

$$\rho_d = (\rho_2 + \rho_1)/2 = \rho_c + D\tau^Z, \quad (3)$$

where  $\rho_c$  is the value of  $\rho$  at the critical point, *D* is the system-dependence parameter, *Z* is the apparent exponent. For a binary mixture there is no prior reason for choosing one “density” variable rather than another, but variables may be examined by testing the symmetry of the coexistence curve and by comparing the goodness of fitting eqn. (3) with  $Z = 1 - \alpha$  and  $2\beta$ ,<sup>2,3</sup> where  $\alpha = 0.11$ <sup>4</sup> characterizes the divergence, as the critical point is approached, of the heat capacity at constant volume for a pure fluid. If the selected “density” variable is not a proper one, the contribution of the  $\tau^{2\beta}$  term to  $\rho_d$  is significant and the fit with  $\tau^{2\beta}$  is significantly better.<sup>5</sup>

Recently, we derived power-law dependence of critical amplitudes on molar mass for coexistence curve, correlation length and susceptibility from a Landau–Ginsburg–Wilson type model for binary solutions with one component being a

small or polymer chain molecule.<sup>6</sup> This derivation was based on a Flory–Huggins expression of free energy of mixing per *n*-mer:

$$F = kT\{(\phi/N_1)\ln \phi + [(1 - \phi)/N_2]\ln(1 - \phi) + \phi(1 - \phi)\chi\} \quad (4)$$

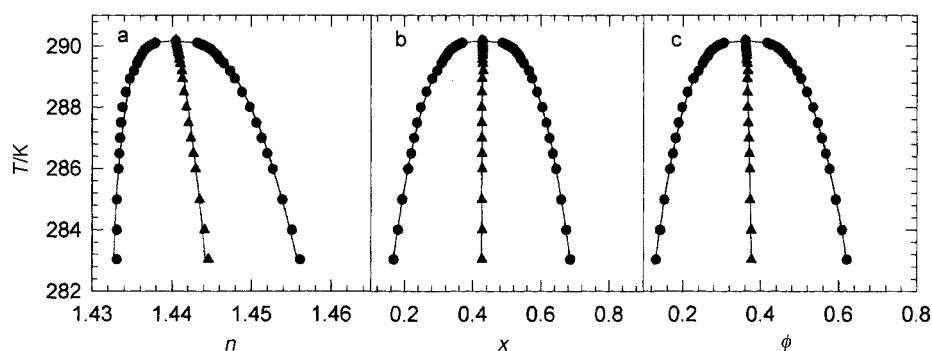
where *k* is Boltzmann’s constant, component 2 represents the chain molecule, *φ* is the volume fraction of component 1,  $\chi$  is a dimensionless interaction parameter, *N<sub>i</sub>* is the chain length of the *i*th component, respectively. *N<sub>2</sub>* is proportional to the molar mass *M<sub>2</sub>* of the chain molecule. However, the molar mass of the chain molecule is obviously not a good variable to describe the critical behaviour of a series of cycloalkane solutions. For example, cycloalkane isomers have different critical volume fractions. On the other hand, according to Scatchard–Hildebrand theory, the free energy of mixing per volume may be expressed as:

$$F = RT\{(\phi/V_1)\ln \phi + [(1 - \phi)/V_2]\ln(1 - \phi) + \phi(1 - \phi)\chi\} \quad (5)$$

where *V<sub>1</sub>* and *V<sub>2</sub>* are the molar volumes of two components. If eqn. (5) is applicable to a series of cycloalkane solutions, then the molar volume of cycloalkane could be a good variable to correlate the properties of those series of hydrocarbon solutions. It would be interesting to investigate the dependence of the critical phenomena on the molar volume fraction for a series of cycloalkane solutions.

In this paper we present precise determinations of critical compositions for four solutions of {*N*-methyl-2-pyrrolidone (NMP) + cycloalkanes} by the equal volume technique<sup>7</sup> and the coexistence curves for (NMP + methylcyclohexane) by measurement of the refractive indices using the method of minimum deviation.<sup>8,9</sup> The experimental results are analysed to determine the critical exponent *β* and the critical amplitude *B*, to examine the behaviour of  $\Delta\rho$  and  $\rho_d$  over a temperature range of 8 K from the critical temperature, and to discuss the

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**Fig. 1** Coexistence curves of: a, temperature against refractive index ( $T, n$ ); b, temperature against mole fraction ( $T, x$ ); and c, temperature against volume fraction ( $T, \phi$ ) for  $\{x\text{NMP} + (1-x)\text{methylcyclohexane}\}$ . ●, Experimental values of concentration variables ( $\rho$ ) of the coexisting phases; ▲, experimental values of diameter ( $\rho_d$ ) of the coexisting phases; —, Concentration variables ( $\rho_{\text{cal}}$ ) of coexisting phases from calculation.

molar volume dependence of critical volume fraction for a series of homogenous cycloalkanes solutions.

## Experimental

NMP (0.99 mass fraction) purchased from Carl Roth Inc. was purified by fractional distillation at decreased pressure. Cyclohexane (0.99 mass fraction) from Beijing Chemical Factory was passed through a column of dried chromatographic alumina and distilled slowly under reduced pressure. The other cycloalkanes (0.99 mass fraction) were supplied by Fluka Chemical Company Inc. All materials were dried and stored over  $4 \times 10^{-10}$  m molecular sieves.

Samples of (NMP + cycloalkanes) were prepared in glass tubes of  $10^{-2}$  m id provided with Ace-thread connectors, which allowed them to be sealed with Teflon caps. Each sample contained an overall volume of about  $2 \times 10^{-6}$  m<sup>3</sup>. The loading mole fractions were determined by weighing and were reproducible to  $\pm 0.002$ . The tubes were placed in a water bath with a temperature stability better than  $\pm 0.002$  K. The temperature difference in the observation area was less than  $\pm 0.002$  K. The critical compositions of the solutions for (NMP + cycloalkanes) were approached by adjusting the ratios of NMP to cycloalkanes to achieve equal volumes of two phases near the critical temperatures.<sup>9</sup> The temperature was measured with a platinum resistance thermometer (WZPB-I, Yunnan Instrument Factory), a precision bridge (QJ69, Shanghai Electrical Instrument Works), and a null detector (ACII-AC 15/2, Shanghai Electric Meter Works). The accuracy and the precision in measurements of the temperature are better than  $\pm 0.01$  and  $\pm 0.002$  K, respectively. From 1 to 5 h was usually required for phases to settle and clarify.

A sample of (NMP + methylcyclohexane) with critical composition was prepared in a rectangular fluorimeter cell provided also with an Ace-thread connector and was used throughout for the measurement of the whole coexistence curve. The phase-separation temperature was carefully determined and taken as the critical temperature. The precision of this measurement was about  $\pm 0.002$  K. It was observed that samples of the same composition had different values of the critical temperature, differing by as much as 0.1 K. Because the critical temperatures of critical solutions are known to be very sensitive to even a minute amount of impurities, this difference might have been a result of uncontrollable impurities introduced into the preparation of the samples. However, it did not affect the final results, because only one sample was used and only the temperature difference ( $T_c - T$ ) was important in data reduction to obtain the critical parameters. The precision in the measurement of ( $T_c - T$ ) is better than  $\pm 0.003$  K. The apparatus for measurements of refractive index was described previously,<sup>9,10</sup> and tested by measuring

the refractive indices of benzene, tetrachloromethane, hexane and cyclohexane at  $T = 293.15$  K and comparing with reference values.<sup>10</sup> The results of comparisons indicate that the accuracy of measurements is better than  $\pm 0.0002$ .

## Results and discussion

The critical temperatures and the critical mole fractions  $x$  for  $\{x\text{NMP} + (1-x)\text{cycloalkanes}\}$  were determined and are listed in columns 2 and 3 of Table 1. The precision in measurements is 0.1 K for the critical temperatures and 0.004 for the critical mole fractions, respectively.

The refractive indices of coexisting phases in the cell for  $\{x\text{NMP} + (1-x)\text{methylcyclohexane}\}$  were measured at various temperatures to obtain a ( $T, n$ ) curve. The results are shown in Fig. 1(a) and are available as supplementary information.<sup>†</sup> The refractive index of a binary solution may be expressed as a linear function of temperature in a certain temperature range by using the following eqns.<sup>10–13</sup>

$$n(T, x) = n(T^0, x) + (\partial n / \partial T)_x (T - T^0), \quad (6)$$

$$(\partial n / \partial T)_x = x(\partial n_A / \partial T) + (1-x)(\partial n_B / \partial T), \quad (7)$$

where  $(\partial n / \partial T)_x$  is the derivative of  $n$  with respect to  $T$  for a particular composition  $x$ ,  $(\partial n_A / \partial T)$  and  $(\partial n_B / \partial T)$  are the values of  $(\partial n / \partial T)_x$  at  $x = 1$  and  $x = 0$ , respectively. A series of the binary solutions with known compositions were prepared and their refractive indices in one phase region at the various temperatures were measured<sup>‡</sup> and fitted with eqns. (6) and (7) to obtain  $(\partial n_A / \partial T)$ ,  $(\partial n_B / \partial T)$  and  $n(T^0, x)$  with a standard deviation of  $2 \times 10^{-4}$  in  $n$ . The value of  $T^0$  was chosen as 284.15 K, the approximate median temperature for coexistence curve determined in this work. The small standard deviation of the fit confirms the validity of eqns. (6) and (7) to

**Table 1** Critical temperatures  $T_c$ , critical mole fractions  $x_c$ , critical volume fractions  $\phi_c$ , and molar volume  $V_2$  at  $T_c$  for  $\{x\text{NMP} + (1-x)\text{cycloalkanes}\}$

Cycloalkane	$T_c/\text{K}$	$x_c$	$\phi_c$	$V_2/\text{cm}^3 \text{ mol}^{-1}$
Cyclohexane	289.2	0.384	0.357	107.57
Methylcyclohexane	290.2	0.435	0.367	127.30
Cyclooctane	291.5	0.453	0.372	133.77
Propylcyclohexane	310.6	0.486	0.385	145.82

<sup>†</sup> Available as supplementary information (SUP 57532; 3 pp.) deposited with the British Library. Details are available from the Editorial Office. For direct electronic access see <http://www.rsc.org/suppdata/cp/1999/2733>.

**Table 2** Values of critical amplitudes  $B$  and critical exponents  $\beta$  in eqn. (2) for coexistence curves of  $(T, n)$ ,  $(T, x)$ ,  $(T, \phi)$  for  $\{x\text{NMP} + (1-x)\text{methylcyclohexane}\}$ 

Order parameter	$(T_c - T) < 1 \text{ K}$		$(T_c - T) < 8 \text{ K}$	
	$B$	$\beta$	$B$	$\beta$
$n$	$0.077 \pm 0.002$	$0.325 \pm 0.004$	$0.076 \pm 0.001$	$0.323 \pm 0.002$
$x$	$1.73 \pm 0.05$	$0.326 \pm 0.004$	$1.73 \pm 0.02$	$0.326 \pm 0.002$
$\phi$	$1.63 \pm 0.05$	$0.326 \pm 0.004$	$1.64 \pm 0.02$	$0.327 \pm 0.002$

(NMP + methylcyclohexane). This allowed us to simplify the procedure for determination of the dependence of  $n$  on  $x$  just by fitting a polynomial form with  $n(T^0, x)$  for various values of  $x$  at  $T^0$ . We obtain the expression:

$$n(T^0, x) = 1.4265 + 0.0339x + 0.0125x^2 \quad (8)$$

with a standard deviation of 0.0002. The values of refractive indices were then converted to mole fractions by calculating  $n(T^0, x)$  through eqns. (6) and (7) and iteratively solving eqn. (8). The results are shown in Fig. 1(b).

The mole fraction was then used to calculate the volume fraction  $\phi$  of NMP by:

$$1/\phi = (1 - k) + k/x, \quad (9)$$

$$k = (d_A M_B)/(d_B M_A), \quad (10)$$

where  $M$  is molar mass,  $d$  is mass density, and subscripts A and B refer to NMP and methylcyclohexane, respectively. The values of densities were obtained from refs. 14 and 15. The values of  $(T, \phi)$  of coexisting phases for this system at various temperatures are shown in Fig. 1(c). The critical mole fractions  $\phi_c$  of four cycloalkane solutions also were converted to the critical volume fractions by using eqns. (9) and (10). The values are listed in column 4 of Table 1.

In the region sufficiently close to the critical temperature, the coexistence curve can be described by eqn. (2). The differences  $(\rho_2 - \rho_1)$  of “density” variables of coexisting phases for  $(T, n)$ ,  $(T, x)$ ,  $(T, \phi)$  were fitted with eqn. (2) and the critical exponent  $\beta$  and critical amplitude  $B$  were obtained. The values depend somewhat on the cutoff values of  $(T_c - T)$  as shown in Table 2. However, for  $(T_c - T) < 1 \text{ K}$ , the exponent  $\beta$  is in good agreement with the theoretical value of (0.3265).<sup>16</sup>

Diameters  $\rho_d$  of coexistence curves for the three choices of the “density” variables were fitted with eqn. (3) to test the significance of the contribution of a  $2\beta$  term and examine the goodness of the selected “density” variables. The apparent exponent  $Z$  in eqn. (3) was fixed at the values  $(1 - \alpha) = 0.89$ , and  $2\beta = 0.653$ , separately. The results are compared in Table 3. The experimental values of  $n_c(\text{expt})$  were obtained by extrapolating refractive indices against temperatures in the one-phase region to the critical temperature. The experimental values of  $x_c(\text{expt})$  were determined by the technique of “equal volume”<sup>7</sup> and the experimental values of  $\phi_c(\text{expt})$  were calculated by eqns. (9) and (10). The values of  $\rho_c$  (i.e.  $n_c$ ,  $x_c$  and  $\phi_c$ )

**Table 3** Parameters of eqn. (3) and standard deviation  $s$  in  $\rho_d$  for diameters of coexistence curves of  $(T, n)$ ,  $(T, x)$ , and  $(T, \phi)$  for  $\{x\text{NMP} + (1-x)\text{methylcyclohexane}\}$ 

	$(T, n)$	$(T, x)$	$(T, \phi)$
$\rho_c(\text{expt})$	$1.4405 \pm 0.0002$	$0.435 \pm 0.004$	$0.367 \pm 0.004$
		$Z = 0.89$	
$\rho_c$	$1.4405 \pm 0.0002$	$0.428 \pm 0.004$	$0.362 \pm 0.004$
$D$	$0.109 \pm 0.001$	$-0.06 \pm 0.01$	$0.40 \pm 0.01$
$s$	$1.1 \times 10^{-4}$	$2.7 \times 10^{-3}$	$2.7 \times 10^{-3}$
		$Z = 0.653$	
$\rho_c$	$1.4402 \pm 0.0002$	$0.428 \pm 0.004$	$0.361 \pm 0.004$
$D$	$0.055 \pm 0.001$	$-0.025 \pm 0.01$	$0.17 \pm 0.01$
$s$	$1.7 \times 10^{-4}$	$2.5 \times 10^{-3}$	$2.2 \times 10^{-4}$

listed in Table 3 were obtained from extrapolation of eqn. (3) to  $\tau = 0$ , and their reported errors include that contributed by converting  $n$  to  $x$ , and  $x$  to  $\phi$ . The extrapolated values are consistent with experimental ones in the experimental uncertainties. The goodness of the fit of eqn. (3) may be indicated by the values of standard deviations  $s$  listed in Table 3. There are almost no differences in  $s$  of the fits with both  $Z = 2\beta$  and  $Z = (1 - \alpha)$  for  $x$  and  $\phi$ . This is consistent with the symmetries of the coexistence curves for  $x$  and  $\phi$ , which are almost identical. Therefore, we are unable to tell which variable,  $x$  or  $\phi$ , is the better choice for the system we studied.

When the critical exponents  $\beta$  and  $\Delta$  were fixed at the theoretical values ( $\beta = 0.3265$ ,  $\Delta = 0.50$ ), eqn. (1) was used to fit phase-separation data to obtain parameters  $B$  and  $B_1$ . The results are listed in Table 4. The first Wegner-correction term  $B_1\tau^{\beta+\Delta}$  is just significant. The uncertainties of parameters listed in Table 4 are the standard deviations from the fitting, which are less than the errors estimated from total experimental uncertainties. The latter is about 2% of the values.

Combination of eqns. (1) and (3) yields:

$$\rho_1 = \rho_c + D\tau^Z - (1/2)B\tau^\beta - (1/2)B_1\tau^{\beta+\Delta}, \quad (11)$$

$$\rho_2 = \rho_c + D\tau^Z + (1/2)B\tau^\beta + (1/2)B_1\tau^{\beta+\Delta}. \quad (12)$$

When  $Z$ ,  $\beta$ ,  $\Delta$  and  $T_c$  were fixed at 0.653, 0.3265, 0.5 and 290.2 K, respectively, and the values of  $D$ ,  $\rho_c$ ,  $B$  and  $B_1$  were taken from Tables 3 and 4, the values of  $\rho_1$ ,  $\rho_2$  and  $\rho_d$  were calculated from eqns. (11), (12), and (3). The results are shown as lines in Fig. 1. The calculated values are in good agreement with experimental results.

By using eqn. (4) and the assumption of  $\chi \propto a/T$ ,<sup>17,18</sup> the symmetric Landau-type expansion of free energy per lattice site around the critical point for chain molecule solutions takes the form:<sup>6,11</sup>

$$f/k = a_1\tau(\phi - \phi_c)^2 + a_2M_2^{0.5}\phi_c^{-2}(\phi - \phi_c)^4, \quad (13)$$

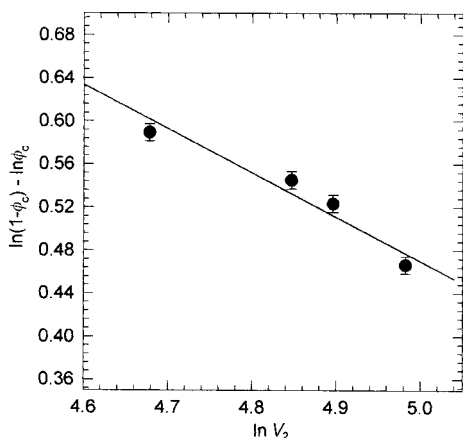
where  $a_1$  and  $a_2$  are unimportant constants independent of  $M_2$  and  $\tau$ . Eqn. (13) yields:

$$(1 - \phi_c)/\phi_c \propto M_2^{-r}, \quad (14)$$

where  $r = 0.5$  is a classical or mean field value. The experimental studies of chain molecule solutions of both small molecules and polymers gave a non-classical universal value of  $r = 0.41$ .<sup>6,19</sup> By using eqn. (5) instead of eqn. (4), the molar volume  $V_2$  of cycloalkanes is substituted for  $M_2$  in eqn. (13),

**Table 4** Values of critical amplitudes  $B$  and  $B_1$  for coexistence curves of  $(T, n)$ ,  $(T, x)$ , and  $(T, \phi)$  in eqn. (1) for  $\{x\text{NMP} + (1-x)\text{methylcyclohexane}\}$ 

Order parameter	$B$	$B_1$
$n$	$0.0776 \pm 0.0002$	
	$0.0784 \pm 0.0004$	$-0.007 \pm 0.003$
$x$	$1.733 \pm 0.003$	
	$1.729 \pm 0.008$	$-0.04 \pm 0.07$
$\phi$	$1.636 \pm 0.003$	
	$1.627 \pm 0.007$	$-0.09 \pm 0.07$



**Fig. 2** A ln–ln plot of  $(1 - \phi_c)/\phi_c$  against molar volume  $V_2$  of cycloalkanes, where  $\phi_c$  is the critical volume fraction of NMP. ●, Experimental values; —, calculated by  $(1 - \phi_c)/\phi_c = 12.43V_2^{-0.41}$ .

and eqn. (14) is modified as:

$$(1 - \phi_c)/\phi_c = CV_2^{-r}, \quad (15)$$

where  $C$  is a proportionality constant. The values of  $V_2$  for four cycloalkanes are listed in column 5 of Table 1, which were calculated from the molar masses and the densities at their critical temperatures. A ln–ln plot of  $\{(1 - \phi_c)/\phi_c\}$  against  $V_2$  for four critical solutions is shown in Fig. 2, where the four points obey well a linear relation. With  $r$  being fixed at 0.41, a least squares fitting gives a value of  $C = 12.43 \pm 0.008$ . The calculated values of  $\{(1 - \phi_c)/\phi_c\}$  by using eqn. (15) with  $r = 0.41$  and  $C = 12.43$  are represented by the solid line in Fig. 2. The standard deviation in  $\phi_c$  was estimated to be 0.003, which is slightly larger than 0.002 of the experimental error in the determination of  $\phi_c$ . It indicates that the four cycloalkanes solutions are possibly in a homogeneous series and the value of  $r$  is likely more universal. If the four solutions studied in this work are really in a homogeneous series and  $V_2$  is a good variable to describe the system dependence of critical behaviour for such a series, then the critical amplitude  $B_\phi$  relating to the coexistence curve with the “density” variable  $\phi$  should be expressed as:<sup>6</sup>

$$B_\phi \phi_c^{-1.865} = AV_m^{-b}, \quad b = 0.29, \quad (16)$$

where  $A$  is a constant. Taking  $B_\phi = 1.636$  from Table 4, we obtained  $A = 43.3$  for (NMP + methylcyclohexane). It would be very interesting to test eqn. (16) for this series of cycloalkanes by further experimental studies of the behaviour of coexisting phases of the remaining three or more cycloalkanes solutions near their critical points.

## Summary

We have measured critical temperatures and critical compositions for binary solutions of {N-methyl-2-pyrrolidone

(NMP) + methylcyclohexane}, (NMP + cyclohexane), (NMP + cyclooctane), and (NMP + propylcyclopentane). The critical volume fractions  $\phi_c$  of those solutions have been found to be dependent on molar volume  $V_2$  of cycloalkane as:  $(1 - \phi_c)/\phi_c = CV_2^{-r}$  with  $C = 12.43$ , and  $r = 0.41$ . The latter was obtained from the experimental studies of chain-molecular solutions. We also determined the coexistence curves for (NMP + methylcyclohexane) in the critical region by measurements of refractive index and proper conversions of refractive index to mole fraction  $x$  and volume fraction  $\phi$ . The scaling exponent  $\beta$  of reduced temperature was extracted from coexistence measurements, and is 0.326, very close to the theoretical value 0.3265. The critical amplitude of coexistence for order parameter  $\phi$  was deduced to be 1.636, which will be used to discuss the molar volume dependence of critical amplitudes of homogeneous cycloalkanes in further work.

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