Journal of Solution Chemistry, Vol. 13, No. 6, 1984

Correlation of the Prigogine-Flory Theory with Isothermal Compressibility and Excess Enthalpy Data for Cyclohexane + Alkane Mixtures

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Received February 3, 1984

The Prigogine-Flory theory is applied to isothermal compressibilities, at 25, 35, 45 and 60°C and to heats of mixing at 25°C for cyclohexane + n-alkane systems. To this purpose, the van der Waals and the Lennard-Jones potentials have been adopted. The energy parameter χ_{12} has been calculated from the experimental data, and its dependence on the n-alkane number of carbons has been studied. Taking the χ_{12} value obtained for the equimolecular mixture, the excess functions $(\partial V^E/\partial P)_T$, H^E and V^E have been calculated and the results compared with experimental values.

KEY WORDS: Excess functions; liquid mixtures; excess volume; excess enthalpy; isothermal compressibility; Prigogine-Flory theory.

1. INTRODUCTION

In previous papers$^{(1,2)}$ the Prigogine-Flory theory has been tested using κ_T data at various temperatures for systems consisting of quasi-spherical molecules. Further testing was made using heat of mixing H^E for mixtures consisting of a small globular aromatic molecule, such as benzene, and an *n*-alkane.$^{(3)}$ In every case, two potentials were selected to express the energy-volume relation. They were the van der Waals potential used by Flory in his original work and the Lennard-Jones potential which is somewhat more complex mathematically. Here we extend this method of testing to cyclohexane + *n*-alkane mix-

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Table I. Parameters for the Pure Components

Solvent	°C	$10^3\alpha^{a,e}$	van der Waals $P^{*\,b}$	van der Waals $V^{*\,c}$	van der Waals $T^{*\,d}$	Lennard-Jones $P^{*\,b}$	Lennard-Jones $V^{*\,c}$	Lennard-Jones $T^{*\,d}$
n-Nonane	25	1.095	445.1	141.73	4982	375.4	143.09	1848
	35	1.111	440.5	142.11	5024	364.4	143.71	1873
	45	1.130	436.9	142.52	5060	854.5	144.39	1896
	60	1.163	431.1	143.09	5109	339.9	145.41	1931
n-Tridecane	25	0.951	459.8	197.90	5380	411.7	198.99	1969
	35	0.963	456.1	198.33	5421	400.4	199.66	1993
	45	0.976	452.8	198.75	5460	389.9	200.34	2016
	60	0.996	449.2	199.44	5519	376.3	201.46	2051
n-Pentadecane	25	0.906	458.7	226.10	5531	419.7	227.07	2016
	35	0.917	459.4	226.55	5571	412.0	227.78	2039
	45	0.929	455.2	227.00	5609	400.3	228.49	2061
	60	0.948	453.4	227.67	5665	387.7	229.61	2095

[a] Units: K^{-1}. [b] Units: J-cm^{-3}. [c] Units: cm-mol^{-1}. [d] Units: K. [e] Obtained from densities reported in Ref. 15.

tures, where the energy interaction is small. In other words, we are using the experimental results obtained in our laboratory to conduct a more exhaustive test of the theory.

2. THEORY

From Prigogine's(4) consideration of molecular degrees of freedom and the division of molecules into segments, Flory *et al.*(5-8) developed a theory for liquid mixtures aimed at predicting their corresponding thermodynamics functions. The theory has undergone successive refinements(9-12) to improve its predicting ability.

In this paper, we consider the excess enthalpy as defined by Flory and the isothermal compressibility as described in previous papers.(1-3)

Depending on the potential selected, the quantity $(\partial V/\partial p)_T$ which is related to κ_T ($\kappa_T = - V^{-1}(\partial V/\partial p)_T$), may be expressed by

$$(\partial V/\partial p)_T = \frac{-3\tilde{q}^{7/3} + 6\tilde{v}^2 - 3\tilde{v}^{5/3}}{-3\tilde{v}^{1/3} + 4} \; \frac{xV_1^* + (1-x)V_2^*}{T(\phi P_1^*/T_1^* + (1-\phi)P_2^*/T_2^*)} \qquad \text{(vdw)} \quad \text{(1a)}$$

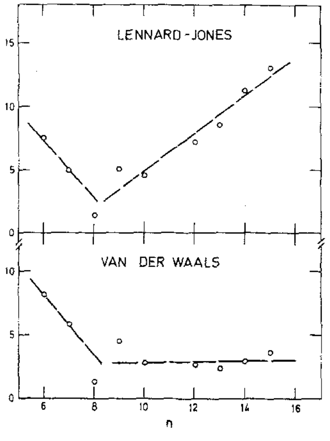

Fig. 1. Plot of χ_{12} at 25 °C for (0.5 C_6H_6 + 0.5 C_nH_{2n+2}) *vs.* the number of carbon atoms *n*.

$$(\partial V/\partial p)_T = \frac{3(-\tilde{v}^2+0.5^{1/6}\tilde{v}^{5/3})}{-6+6(\tilde{v}^2-1)^{-1}+\tilde{v}^{-1/3}(2^{1/6}-\tilde{v}^{-1/3})^{-1}}\,\frac{xV_1^*+(1-x)V_2^*}{T(\phi P_1^*/T_1^*+(1-\phi)P_2^*/T_2^*)} \qquad \text{(LJ)} \quad \text{(1b)}$$

where ϕ is the segment fraction of component 1 and $\tilde{v}$ the reduced volume of the mixture. As described previously,(1,7) the characteristic values P_i^*, V_i^* and T_i^* of the pure substances may be calculated from the molar volume V, the isothermal compressibility κ_T and the isobaric thermal expansion coefficient $\alpha = V^{-1}(\partial V/\partial T)_p$. The χ_{12} parameter for each potential may be obtained from κ_T data as described in Ref. 3, using Flory's(6) relationship

$$P^* = \phi P_1^* + (1-\phi)P_2^* - \phi\theta_2\chi_{12} \qquad (2)$$

where θ_2 is the surface fraction obtained using Bondi's(13) molecular surfaces.

The corresponding expressions for H^E are given by

Table II. Coefficients and Standard Deviations for Eq. (5) for Several Systems

°C	$10^{-3}A_0$	$10^{-3}A_1$	$10^{-3}A_2$	$10^{-3}A_3$	s^a
Cyclohexane (1) + *n*-Hexane (2)					
25	-220.14	115.67	-21.08	3.75	0.37
35	-245.97	131.97	-23.48	3.32	0.21
45	-275.26	150.64	-22.38	-1.46	0.35
60	-330.21	195.57	-42.14	4.13	0.39
Cyclohexane (1) + *n*-Heptane (2)					
25	-211.97	91.99	-1.94	---	0.35
35	-233.89	103.33	-3.95	---	0.48
45	-258.89	114.36	-3.99	---	0.31
60	-302.93	133.24	-3.01	---	0.31
Cyclohexane (1) + *n*-Octane (2)					
25	-208.98	87.00	---	---	0.39
35	-229.00	94.55	---	---	0.39
45	-251.14	102.29	---	---	0.59
60	-290.07	116.93	---	---	0.71
Cyclohexane (1) + *n*-Nonane (2)					
25	-211.31	82.08	7.35	---	0.33
35	-230.42	87.97	8.67	---	0.57
45	-250.80	92.78	9.48	---	0.30
60	-286.49	104.87	8.77	---	0.33
Cyclohexane (1) + *n*-Decane (2)					
25	-214.46	86.01	6.63	---	0.19
35	-232.79	91.93	6.69	---	0.29
45	-253.06	91.57	6.16	---	0.22
60	-286.97	106.42	7.71	---	0.26
Cyclohexane (1) + *n*-Dodecane (2)					
25	-225.45	97.01	6.68	---	0.25
35	-242.78	103.47	5.00	---	0.21
45	-262.73	109.02	5.26	---	0.21
60	-295.97	116.63	6.63	---	0.16
Cyclohexane (1) + *n*-Tridecane (2)					
25	-231.25	103.96	5.55	---	0.20
35	-349.93	108.51	7.17	---	0.27
45	-270.12	116.65	5.00	---	0.18
60	-302.02	121.87	7.39	---	0.31

Table II. Continued

°C	$10^{-3}A_0$	$10^{-3}A_1$	$10^{-3}A_2$	$10^{-3}A_3$	s^a
		Cyclohexane (1) + *n*-Tetradecane (2)			
25	-238.56	110.95	5.85	---	0.30
35	-256.56	116.79	5.50	---	0.33
45	-276.60	121.57	6.78	---	0.29
60	-309.54	130.70	6.11	---	0.19
		Cyclohexane (1) + *n*-Pentadecane (2)			
25	-246.67	119.38	5.54	---	0.12
35	-263.66	122.65	6.86	---	0.26
45	-284.98	130.20	6.38	---	0.30
60	-316.95	137.00	7.15	---	0.41

[a] Units: $\mathrm{cm^3\text{-}mol^{-1}\text{-}TPa^{-1}}$.

$$H^E = xV_1^*P_1^*/\tilde{v}_1 + (1\text{-}x)V_2^*P_2^*/\tilde{v}_2 - P^*V^*/\tilde{v} \qquad \text{(vdw)} \quad (3a)$$

$$H^E = xV_1^*P_1^*(-2\tilde{v}_1^{-2} + \tilde{v}_1^{-4}) - (1\text{-}x)V_2^*P_2^*(-2\tilde{v}_2^{-2} + \tilde{v}_2^{-4}) + P^*V^*(-2\tilde{v}^{-2} + \tilde{v}^{-4}) \qquad \text{(LJ)} \quad (3b)$$

where χ_{12}, intervening implicitly through P^*, may be obtained from H^E data.

Another thermodynamic quantity used to test theories of liquids is V^E giving by

$$V^E = \tilde{v}[xV_1^* + (1\text{-}x)V_2^*] - xV_1 - (1\text{-}x)V_2 \qquad (4)$$

Thus the advantage of the Prigogine-Flory theory is that the excess functions may be calculated using V, α and κ_T values of the pure substances. However, the theory requires a unique χ_{12} value for each system, whatever property is used to calculate it, something that does not happen in practice. Consequently, a good test of the theory could be achieved by calculating χ_{12} from two different properties such as κ_T and H^E.

3. RESULTS AND DISCUSSION

The experimental values of κ_T and ρ at 25, 35, 45 and 60 °C for the pure substances have been published.(14) In Table I are gathered α,

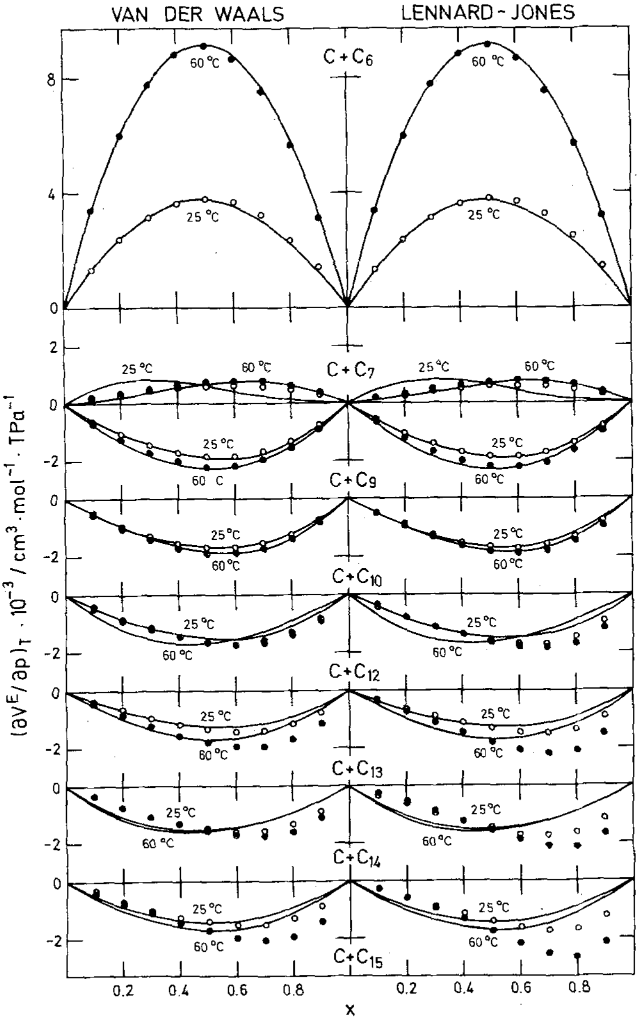

Fig. 2. $(\partial V^E/\partial p)_T$ vs. mole fraction benzene: ——, experimental values; ○ (at 25 °C) and ● (at 60 °C), theoretical values.

P^*, V^* and T^* values we have obtained for *n*-nonane, *n*-tridecane and *n*-pentadecane. The corresponding values for the other substances have been reported previously.(1,3) Measurements of κ_T at the temperatures referred to were carried out in our laboratory for cyclohexane + *n*-alkane binary mixtures from *n*-hexane to *n*-pentadecane.(14) For each mixture, the quantity $(\partial V/\partial p)_T$ as a function of the cyclohexane mole fraction x, was fitted to a polynomial

$$(\partial V/\partial p)_T = \sum_{i=0}^{n} A_i x_i \tag{5}$$

whose coefficients A_i and standard deviations s are given in Table II. Substituting $(\partial V/\partial p)_T$ in Eq. (1) and following the procedure described in Ref. 3, the χ_{12} values for nine mole fractions were obtained and are gathered in Table III for the equimolecular mixtures and for both potentials and at each of the four mentioned temperatures. Comparing these values with those for benzene + *n*-alkane(3) systems, we may conclude that the χ_{12} parameter is smaller in mixtures of chemically similar components, such as non-aromatic + non-aromatic (cyclohexane + *n*-alkane) than in more energy interacting systems, such as aromatic + non-aromatic (benzene + *n*-alkane).

Figure 1 is a plot of χ_{12} at 25 ℃ against the *n*-alkane carbon number *n*. This has been done for both potentials and of course it could have been shown at any other temperatures. The variation of χ_{12} with *n* is similar to that obtained for benzene + *n*-alkane but χ_{12} is smaller for the same *n*. For both potentials χ_{12} decrease with increasing *n* up to the cyclohexane + *n*-octane system. For higher *n*, χ_{12} slightly increases with *n* for the van der Waals potential with the increase much larger for the Lennard-Jones potential.

The theory has been tested using the $\chi_{12}(\kappa_T)$ values in Table III by calculating three excess functions: $(\partial V^E/\partial p)_T = -\kappa_T^E$ from

$$(\partial V^E/\partial p)_T = (\partial V/\partial p)_T - x(\partial V_1/\partial p)_T - (1-x)(\partial V_2/\partial p)_T \tag{6}$$

where $(\partial V/\partial p)_T$ is obtained through Eq. (1), H^E is calculated from Eq. (3) and V^E from Eq. (4).

Experimental and calculated $(\partial V^E/\partial p)_T$ values *vs.* x at 25 and 60 ℃ are plotted in Fig. 2. The experimental and calculated values are very close with any of the two potentials and at the four temperatures, even though the χ_{12} values are different for each. It is possible to predict the sign change of the excess function around the cyclohexane + *n*-octane region. The deviations for the last three systems and at greater cyclohexane concentrations are caused by χ_{12} variations with composition.

The experimental H^E values and those calculated from $\chi_{12}(\kappa_T)$ at 25 ℃ are represented on Fig. 3. With a van der Waals potential there is a good agreement for the cyclohexane + *n*-hexane system but for the other systems the experimental and the calculated values disagree. Moreover, the theoretical variation of H^E with *n* is not the correct one. However, with a L-J potential, predicted H^E values are correct for the

Table III. Values of the Flory Parameter obtained from κ_T and H^E Measurements

	χ_{12}			
	25 °C	35 °C	45 °C	60 °C
	Cyclohexane (1) + *n*-Hexane (2)			
vdW	8.2 (9.1)[b]	8.0	6.7	5.5
LJ	7.6 (8.0)[b]	7.1	5.9	4.7
	Cyclohexane (1) + *n*-Heptane (2)			
vdW	5.9	4.7	4.8	5.5
LJ	5.0	3.8	3.8	4.0
	Cyclohexane (1) + *n*-Octane (2)			
vdW	1.3 (9.6)[b]	1.2	0.8	0.2
LJ	1.4 (8.4)[b]	1.3	0.9	0.4
	Cyclohexane (1) + *n*-Nonane (2)			
vdW	4.5	4.0	3.9	2.4
LJ	5.1	4.7	4.5	3.2
	Cyclohexane (1) + *n*-Decane (2)			
vdW	2.8 (10.7)[b]	1.9	1.0	1.2
LJ	4.7 (9.6)[b]	4.0	3.3	3.5
	Cyclohexane (1) + *n*-Dodecane (2)			
vdW	2.6	1.4	1.8	2.6
LJ	7.2	6.2	6.6	7.2
	Cyclohexane (1) + *n*-Tridecane (2)			
vdW	2.4 (13.2)[b]	3.5	2.3	4.6
LJ	8.6 (12.3)[b]	9.7	8.4	10.1
	Cyclohexane (1) + *n*-Tetradecane (2)			
vdW	3.0 (14.0)[b]	3.2	4.6	5.6
LJ	11.2 (13.2)[b]	11.2	12.2	12.5
	Cyclohexane (1) + *n*-Pentadecane (2)			
vdW	3.6 (15.2)[b]	5.4	5.4	7.9
LJ	13.0 (14.4)[b]	14.6	14.3	15.8

[a] Units: J-cm^{-3}. [b] Obtained from H^E values of Ref. 16.

first and last systems. Also variation of H^E with n is correct from the cyclohexane + *n*-octane system on because χ_{12} increases with n and on account of the great sensitivity of H^E to χ_{12}. From that system on H^E

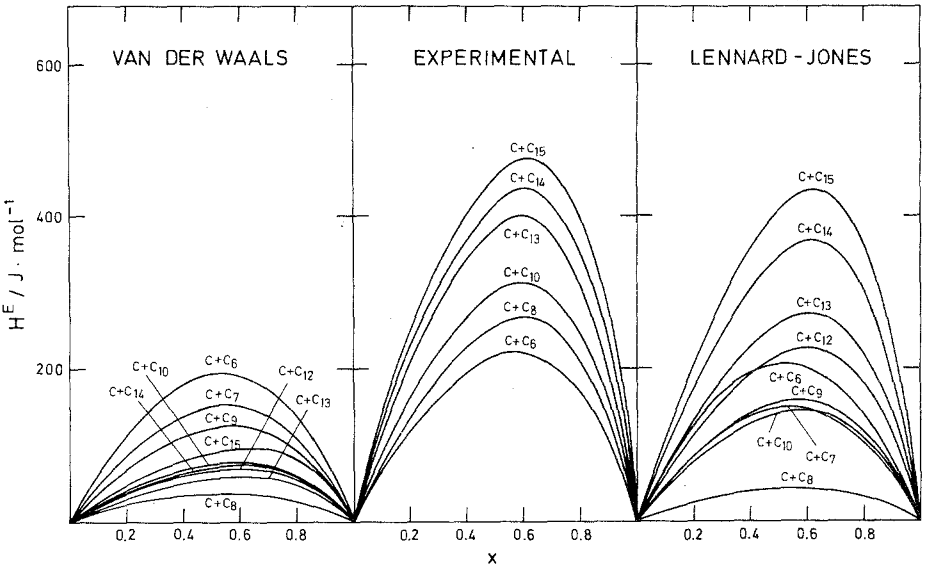

Fig. 3. Comparison of experimental and theoretical values of H^E obtained from χ_{12} (κ_T) at 25 °C.

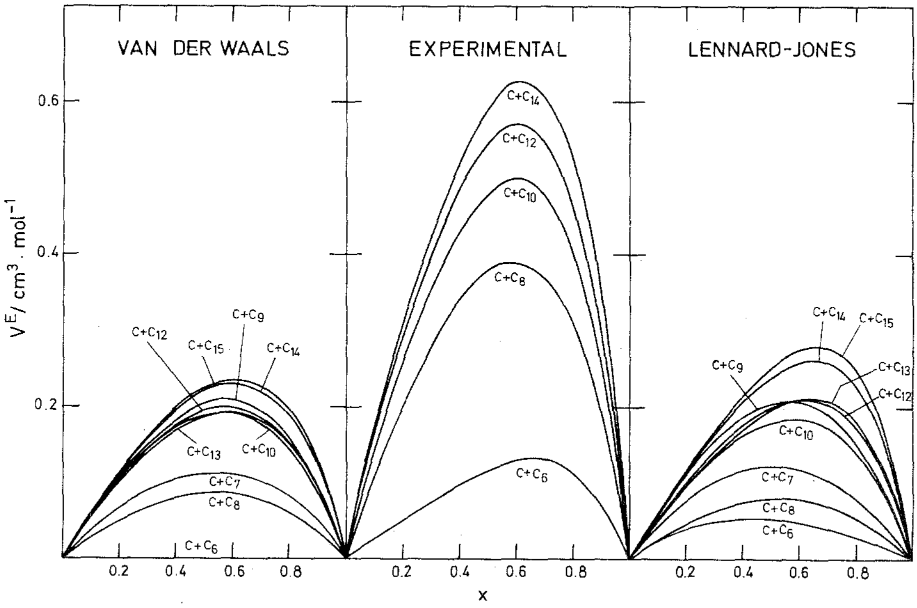

Fig. 4. Comparison of experimental and theoretical values of V^E obtained from χ_{12} (κ_T) at 25 °C.

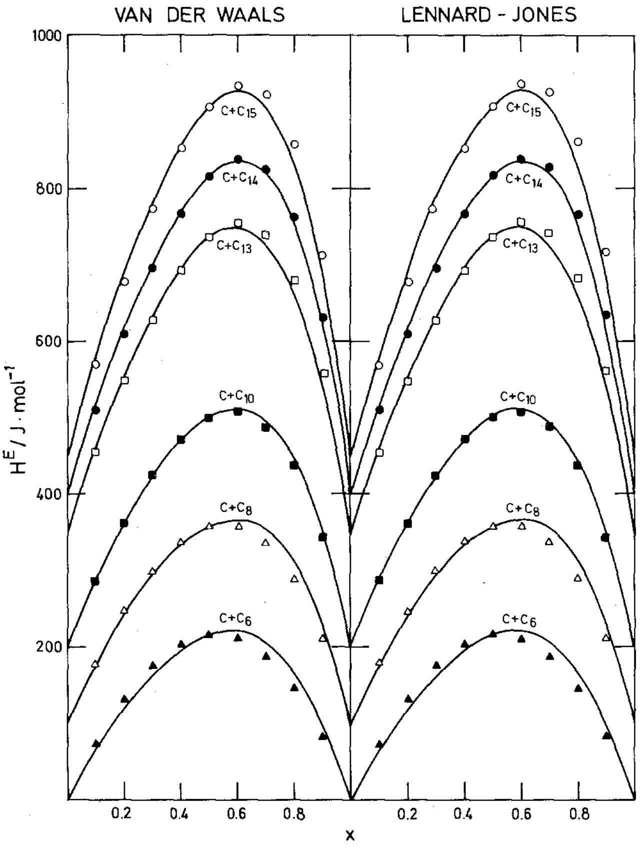

Fig. 5. Values of H^E at 25 °C: ——, experimental values; symbols, theoretical values.

increases properly with chain length with the result that H^E predictions with a L-J potential are better than with a vdW potential.

The corresponding plot for V^E at 25 °C is shown in Fig. 4. Both potentials give similar results which are lower than the experimental data.(17) Perhaps there is a slight advantage with the L-J potential. With it, the increase of V^E with n is nearly correct although $\chi_{12}(\kappa_T)$ shows a minimum. All this confirms the close correlation between χ_{12} and H^E but not between χ_{12} and V^E. This is as it should be since χ_{12} represents the molecular interaction between the mixture components.

A discussion of the theory could be conducted by substituting in Eq. (3) the H^E data(16) for the same series of systems determined by us at 25 °C. The χ_{12} values obtained are in parentheses in Table III. The theoretical values fit well for any potential with the experimental

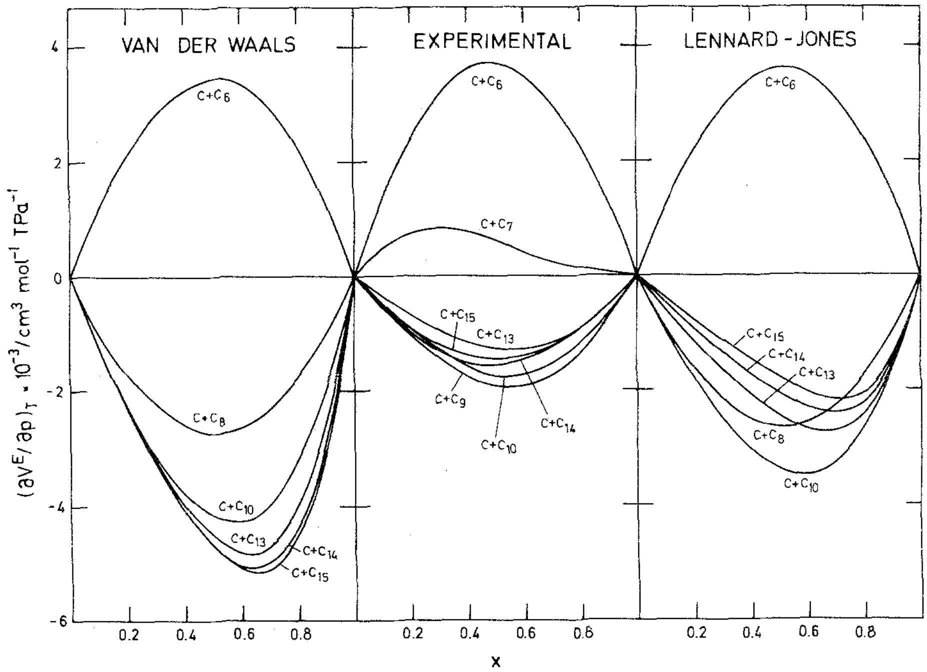

Fig. 6. Comparison of experimental and theoretical values of $(\partial V^E/\partial p)_T$ obtained from $\chi_{12}\ (H^E)$ at 25 °C.

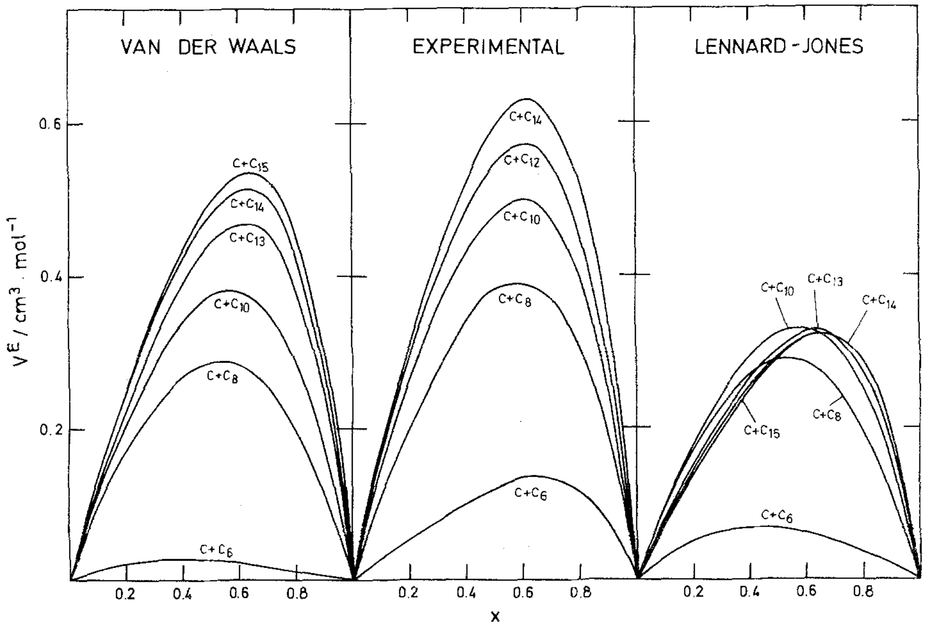

Fig. 7. Comparison of experimental and theoretical values of V^E obtained from $\chi_{12}\ (H^E)$ at 25 °C.

data as can be observed in Fig. 5. Starting with *n*-hexane, in Fig. 5 the origin of H^E has been increased 50 J-mol^{-1} per carbon atom of the *n*-alkane.

The experimental and calculated values of $(\partial V^E/\partial p)_T$ at 25 °C are represented in Fig. 6. Both potentials are adequate in giving the positive value of that excess function for the cyclohexane + *n*-hexane system and the negative value for the other systems in agreement with the experimental results. An exception is the cyclohexane + *n*-octane system, whose excess compressibility is close to zero. The $(\partial V^E/\partial p)_T$ values are better reflected with an $\chi_{12}(H^E,\text{L-J})$ but their variation with n is shown better by $\chi_{12}(H^E,\text{vdw})$. However, the best success of the theory is in predicting the sign change of $(\partial V^E/\partial p)_T$ between the cyclohexane + *n*-hexane and the cyclohexane + octane systems in particular if one keeps in mind the extremely low value of this excess function.

The V^E values calculated from $\chi_{12}(H^E)$ are compared at 25 °C with the experimental ones on Fig. 7. Both potentials give the right sign for V^E but the numerical value is reproduced better by a vdw potential. Furthermore, this potential gives good agreement with the experimental results of V^E variation with *n*-alkane chain length.

In summary, the conclusion is that the theory reproduces $(\partial V^E/\partial p)_T$ and H^E values adequately if they are calculated, respectively, from $\chi_{12}(\kappa_T)$ and $\chi_{12}(H^E)$. This is true with either of the two potentials. Starting with κ_T data the L-J potential gives better results for the other excess functions H^E and V^E, while starting from H^E measurements prediction of $(\partial V^E/\partial p)_T$ and V^E is definitely better with a vdW potential. This conclusion is in line with a previous test of the theory for the benzene + *n*-alkane systems.$^{(3)}$

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