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PHASE EQUILIBRIA FOR STRONGLY NONIDEAL MIXTURES FROM AN EQUATION OF STATE

WITH DENSITY-DEPENDENT MIXING RULES

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Abstract

An equation of state of the van der Waals form represents vapor-liquid and liquid-liquid equilibria in binary, particularly aqueous, mixtures. The Mansoori-Carnahan-Starling expression is used for the repulsive part of the equation of state while the attractive part uses a simple van der Waals form. For a mixture, the usual (density-independent) quadratic mixing rule is used for the leading attractive term but a density-dependent correction is added to allow for noncentral intermolecular forces of dissimilar components at high densities. This procedure gives the necessary quadratic dependence of the second virial coefficient at low densities but includes also cubic terms for representation of phase equilibria at liquid-like densities. Good results are obtained for vapor-liquid and liquid-liquid equilibria in binary systems containing water, hydrocarbons, phenol, pyridine and methanol. However, extension to liquid-liquid equilibria in ternary systems is not successful because the equation of state is not able properly to represent phase equilibria of binary systems at conditions only slightly removed from binary liquid-phase instability; at these conditions, the equation of state erroneously predicts a two-liquid region. For further progress toward application of equations of state to ternary liquid-liquid equilibria, it will be necessary to introduce some fundamental modifications toward better represen-tation of phase behavior in the critical region.

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Recent research has shown that equations of state for dense fluid mixtures often give poor results for phase-equilibrium calculations because the one-fluid approximation, coupled with quadratic mixing rules, provides a good model only for simple mixtures where the molecules do not differ appreciably in size; however, in the dilute region, it appears that the one-fluid theory is never reliable, not even for simple mixtures, unless all molecules are of the same size (Shing and Gubbins, 1983).

Several authors (Mollerup, 1981; Whiting and Prausnitz, 1982; Mathias and Copeman, 1983) have suggested that better results could be obtained if, in a chosen equation of state, we allow the constants to depend not only on composition (which is the essence of one-fluid theory) and, perhaps, on temperature (which is consistent with one-fluid theory), but also on density, subject to the restriction that for a pure component, no change is introduced into the chosen equation of state. This suggestion leads to the concept "density-dependent mixing rules" which provides a promising new procedure for phase-equilibrium thermodynamics. This procedure appears to be particularly attractive for applying equations of state toward calculation of phase equilibria for strongly nonideal fluid mixtures, including those with liquid-liquid miscibility gaps.

In this work we present a procedure for semi-empirical development of density-dependent mixing rules toward phase-equilibrium calculations, including three-phase (vapor-liquid-liquid) calculations. After a general discussion, we present some results for several strongly nonideal aqueous mixtures. While our results indicate significant improvement over those that can be obtained using conventional equation-of-state methods, it is clear that better density-dependent mixing rules remain to be established for

satisfactory representation of phase equilibria in complex mixtures.
Further, it appears that some fundamental modifications in the equation of state
are required when calculations are made for those ternary liquid-liquid equilibria
where the binodal curve has a plait point.

Helmholtz Energy for an Equation of State of the van der Waals Form

Consider a van der Waals-type mixture containing n_1 moles of component 1,
n_2 moles of component 2, etc. at temperature T and total volume V. The number
of components is m. The Helmholtz energy A is given by

$$A = \sum_{i=1}^{m} n_i \underline{a}_i^0 + \sum_{i=1}^{m} n_i RT \ln(n_i RT/V) + \Delta A^{rep} - (n_T^2 a^H/V) \Theta(\xi) \tag{1}$$

where $\underline{a}_i^0$ is the Helmholtz energy of pure i in the ideal-gas state at T and
unit pressure (here taken as 1 bar), n_T is the total number of moles and a^H
is the van der Waals "constant" which, in general, depends on temperature,
composition and (using density-dependent mixing rules) on density.
Superscript H is to remind us that this "constant" is for the Helmholtz
energy; to find the corresponding a^{EOS} for the equation of state, we use the
standard relation

$$P = - (\partial A/\partial V)_{T, \text{all } n_i} \tag{2}$$

In Equation (1), Θ is a simple algebraic function of reduced density ξ as
indicated in Table 1; in the simplest case (original van der Waals
equation), $\Theta = 1$.

In Equation (1), ΔA^{rep} is the contribution of repulsive forces, usually obtained from a "hard-sphere" equation of state which depends on molecular diameters σ_1, σ_2, σ_3 etc., in addition to temperature, density and composition. Table 2 gives two expressions for ΔA^{rep}; one of these is based on the original van der Waals equation and the other on the extension to mixtures (Mansoori et al., 1971) of the expression proposed by Carnahan and Starling (1969). Other expressions, for convex hard bodies, have been proposed by several authors (Naumann et al., 1981; Boublik, 1981) but we shall not consider these here.

Shing and Gubbins (1983) have shown convincingly that for dilute solutions, the common one-fluid (or two-fluid) van der Waals approximations do not give good results for those mixtures where there is a significant difference in molecular size. Therefore, we use the expression of Mansoori-Carnahan-Starling rather than van der Waals n-fluid theory.

For simple mixtures, van der Waals constant a^H, independent of density, is a quadratic function of mole fraction x as suggested empirically many years ago and as derived from perturbation theory (Henderson, 1979). This quadratic dependence is necessary at low densities because the second virial coefficient B must be quadratic in mole fraction (Prausnitz, 1969):

$$B = \sum_i^m \sum_j^m x_i x_j \, B_{ij} \tag{3}$$

where

$$B_{ij} = 4b_{ij} - a_{ij}^{EOS}/RT \tag{4}$$

Here $b_{ij} = (\pi/6) N_{Av} [(\sigma_i + \sigma_j)/2]^3$ where N_{Av} is Avogadro's number.
For "soft" spheres, b_{ij} may be slightly temperature dependent but,
in any event, experimental data clearly show that a_{ij}^{EOS} is temperature
dependent such that a_{ij}^{EOS} approaches a constant at high temperature but
rises with reciprocal temperature, usually with increasing slope.

If the mixing rule for a^H is independent of density, then Equations (3)
and (4) force us to the conclusion that, regardless of density,

$$a^H = \sum_{i}^{m} \sum_{j}^{m} x_i x_j \, a_{ij}^H \tag{5}$$

Theory and experiment suggest that Equation (5) is satisfactory for low
and high fluid densities provided that molecules i and j are nonpolar and
spherical, in other words, provided that the intermolecular forces are
central (no orientations). To apply Equation (1) to mixtures whose
molecules exhibit noncentral (as well as central) forces, we suggest
an extension of Equation (5):

$$a^H = \sum_{i}^{m} \sum_{j}^{m} x_i x_j \, a_{ij}^H + a^{H,nc} \tag{6}$$

where the last term represents the contribution to a^H of noncentral forces
for all unlike i-j pairs; superscript nc refers to noncentral forces.

We can rewrite Equation (6) in a more explicit form but for simplicity
we now drop superscript H, it being understood that we are considering the
van der Waals "constant" in Equation (1). Instead of Equation (6), we write

$$a = \sum_{i}^{m} x_i a_{ii} \quad + \quad (1/2) \sum_{i \neq j}^{m} \sum^{m} x_i x_j (2a_{ij} - a_{ii} - a_{jj}) \quad + \quad a^{nc} \qquad (7)$$

| [contribution from ideal mixing] | [contribution from central forces to nonideal mixing] | [contribution from noncentral forces to nonideal mixing] |

We know little about a^{nc} but we can specify two boundary conditions. First, remembering that a^{nc} refers only to noncentral contributions from <u>unlike</u> pairs,

$$a^{nc} \to 0 \quad \text{as } x_i \to 1 \qquad (8)$$

Second, we expect that as temperature rises or as density falls, the importance of noncentral forces must decline; therefore,

$$a^{nc} \to 0 \quad \text{as } \rho/RT \to 0 \qquad (9)$$

where density $\rho = n_T/V$.

Finally, experimental data for numerous mixtures indicate that at high densities, quadratic dependence on mole fraction is insufficient. We therefore suggest for a^{nc} the <u>simplest</u> approximation consistent with our boundary conditions:

$$a^{nc} = (\rho/RT) \sum_{i \neq j}^{m} \sum^{m} x_i x_j (x_i c_{i(j)} + x_j c_{j(i)}) \qquad (10)$$

where $c_{i(j)}$ is a binary parameter that reflects noncentral forces when molecule j is infinitely dilute, surrounded by molecules i; $c_{j(i)}$ has a similar significance with i and j interchanged.

In Equation (7), we follow customary practice by writing

$$a_{ij} = (a_{ii} \, a_{jj})^{1/2} \, (1-k_{ij}) \tag{11}$$

where $k_{ii} = k_{jj} = 0$ and where the magnitude of binary parameter k_{ij} ($i \neq j$) is usually small compared to unity. We then obtain for van der Waals "constant" a in Equation (7):

$$a = \sum_i^m \sum_j^m x_i x_j \, (a_{ii} a_{jj})^{1/2} \, (1-k_{ij}) + (\rho/RT) \sum_i^m \sum_{j \atop i \neq j}^m x_i x_j (x_i c_{i(j)} + x_j c_{j(i)}) \tag{12} \; *)$$

Equations (1) and (12) are similar to relations proposed by Mathias and Copeman (1983) who used the Peng-Robinson equation of state for ΔA^{rep} and for $\Theta(\xi)$. However, in detail Mathias and Copeman's result is different from ours and their derivation follows from different assumptions. In the following discussion we apply Equations (1) and (12) to binary data. Consistent with our intention to maintain simplicity, we set $\Theta(\xi) = 1$.

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*) For a binary mixture,

$$a = x_1^2 a_{11} + x_2^2 a_{22} + 2x_1 x_2 [(a_{11} a_{22})^{1/2}(1-k_{12})+(\rho/RT)(x_1 c_{1(2)}+x_2 c_{2(1)})]$$

Correlation of LLE of Hydrocarbon-Water Systems

Equations (1) and (12) have been applied to pure water, to pure hydrocarbons, to phenol, pyridine, methanol and to some of their mixtures. Pure-component parameters are obtained by fitting liquid saturation pressures and liquid densities for temperature ranges shown in Table 3b. (Timmermans, 1950; Connolly and Kandalic, 1962; API Research Project 44, 1973; Kratzke et al., 1984; Bain, 1964; Zubarev et al., 1973; Wilhoit and Zwolinski, 1973). Supercritical PVT data were also used for methane and propane (IUPAC, 1976; Goodwin, 1977). Pure-component parameters a_{ii} and b_i were adjusted separately for each temperature; for the range of interest here, the temperature dependences of a_{ii} and b_i can be represented by the linear relations

$$a_{ii}(T) = \alpha_i - \beta_i T \tag{13a}$$
$$b_i(T) = \gamma_i - \delta_i T \tag{13b}$$

where T is in K. Table 3a gives constants α_i, β_i, γ_i and δ_i and Table 3b gives details concerning the goodness of fit.

Pure-component parameters were used to correlate binary vapor-liquid (VLE) and liquid-liquid equilibria (LLE) with three temperature-independent binary parameters k_{12}, $c_{1(2)}$ and $c_{2(1)}$ according to Equation (12). Figures 1 to 6 compare experimental and calculated mutual solubilities; Table 4 shows the binary parameters. Agreement between calculated and experimental LLE is remarkably good considering the simplicity of the correlating equation and the experimental scatter; Figures 1 to 6 show smoothed experimental results.

While temperature-independent binary parameters are satisfactory for LLE remote from the critical region, these parameters overestimate the two-liquid region as shown in Figure 6. Agreement with experiment in the critical region can be achieved by assigning a temperature dependence to the binary parameters but such agreement is necessarily no more than a forced fit devoid of physical significance.

While temperature-independent binary parameters appear to be satisfactory for LLE for aqueous systems remote from critical conditions and for LLE and VLE for water-propane (Figure 7), it was not possible to use such parameters for VLE in the system water-methane. For this highly asymmetric system where the volatilities of the two components differ widely, it appears that the mixing rules proposed here [Equation (12)] are not adequate. If we allow the binary parameters to vary systematically with temperature, we can obtain a good fit, as shown in Figure 8. However, such a forced fit has little if any physical significance. We nevertheless include Figure 8 here to call attention to the limitations of Equation (12) which, as stressed earlier, gives only a first correction to the simple quadratic mixing rule for van der Waals "constant" a.

Although Equation (12) appears to be suitable for the high-density region, it is consistent with the low-density limit of a quadratic second virial coefficient. Therefore, binary parameter k_{12}, obtained from fitting LLE data, should provide a reasonable second virial cross coefficient according to Equation (4). Table 5 shows experimental and

calculated second virial cross coefficients for three binary aqueous systems where reliable experimental results are available; in every case, calculations are based on results obtained from high-density binary data. Predicted B_{12}'s are in reasonable agreement with experiment but it is evident that k_{ij} obtained from high-density binary data is not identical to an optimum k_{ij} for fitting low-density binary data.

An alternate way to fit the binary LLE data is first to determine k_{12} from second-virial-coefficient (B_{12}) data and then to fit $c_{1(2)}$ and $c_{2(1)}$ from the LLE data. When this is done, the results are not satisfactory unless $c_{1(2)}$ and $c_{2(1)}$ are allowed to vary with temperature.

It is likely that since Equation (12) uses the simplest correction to the quadratic mixing rule, it is not satisfactory for both low and high densities. It may be that the density dependence in Equation (12) is too weak to separate high-density and low-density effects on a. It may be better to use a continuous switching function of density as suggested by Dimitrelis (1982); this switching function would give a quadratic mixing rule at low density and a cubic mixing rule at high density but the transition from one to the other would be given by an S-shaped function of density rather than by the truncated polynomial in density in Equation (12).

It appears that, while a density-dependent mixing rule is promising for better representation of fluid-phase equilibria of asymmetric mixtures, Equation (12) gives only a first approximation toward that end.

However, Equation (12) presents another, more fundamental, difficulty which becomes evident when we consider ternary mixtures. While Equation (12) gives good results for binary VLE and LLE, utility for engineering work requires that it also be useful for ternary (and higher) systems. While there are no serious problems for ternary VLE, we find that we cannot, in general, use Equation (12) for ternary LLE. To illustrate this limitation, we considered two ternary systems near room temperature:

I   Methanol - Benzene - Water

II Pyridine - Benzene - Water

In systems I and II, there are two completely miscible binaries (methanol-benzene, methanol-water; pyridine-benzene, pyridine-water) and one partially miscible binary (benzene-water). Therefore the connodal line for both ternaries is continuous with a plait point. As shown earlier, there is no problem in fitting LLE data for the benzene-water binary with Equation (12). There is also no problem in fitting VLE data for the miscible binaries. But Equation (12) cannot fit LLE data for the two ternaries.

Optimum binary parameters for the totally miscible binaries are shown in Table 6. These binary parameters are physically reasonable for the last three binary systems but k_{12} is not reasonable for the first one; for that binary, when a reasonable k_{12} is used, it was not possible to obtain a good fit for the binary VLE data.

When we tried to fit ternary LLE data using binary parameters only, we were not successful. However, when we include also a few adjustable ternary parameters (Cha and Prausnitz, 1984), we were also unsuccessful.

The reason for our failure to fit ternary LLE data becomes clear when we notice that the VLE data for two of the completely miscible binaries (methanol-benzene and pyridine-water) indicate conditions close to liquid-phase instability. Although it was possible to fit the binary VLE data for these two systems, we found that the optimum binary parameters erroneously predict that the binary liquid phase is not stable; these binary parameters erroneously yield an immiscible binary liquid-liquid region with solubility limits shown in Table 7. It is therefore, in principle, not possible to fit the ternary LLE data (even when ternary parameters are used) because the calculations produce a partially miscible region for each of the two binaries shown in Table 7, contrary to observation.

It is well known that typical equation-of-state calculations for binary systems yield upper critical solution temperatures which are too large (as indicated in Figure 6); in other words, the calculations produce a two-phase (liquid-liquid) region at temperatures where, in fact, there is only one liquid phase. Many authors have shown that equations of the van der Waals form are not reliable in the critical region; therefore, when an equation of that form is used to calculate a ternary LLE diagram where one of the constituent binaries is only slightly above its upper critical solution temperature, the calculations are qualitatively incorrect. We conclude that further progress in calculating ternary LLE requires attention to the problem of properly representing equilibria in the critical region. This is a difficult fundamental problem which has been discussed by physicists for some time but which, as yet, has received little attention from chemical engineers.

Acknowledgment

Table 1

EXPRESSIONS FOR $\Theta(\xi)$ in Equation (1); $\xi = n_T\, b/V$

Equation of State	$\Theta(\xi)$
original van der Waals	1
Redlich-Kwong	$[\ln(1 + 4\xi)]/4\xi$
Peng-Robinson	$\left\{ \ln \dfrac{1 + (1+\sqrt{2})4\xi}{1 + (1-\sqrt{2})4\xi} \right\} \dfrac{1}{8\sqrt{2}\,\xi}$

Table 2

EXPRESSIONS FOR ΔA^{rep} IN EQUATION (1)

$$\xi = \sum_{i=1}^{m} \xi_i \ , \quad \xi_i = (\pi/6)(n_T N_{Av}/V) x_i \sigma_i^3$$

$$\xi = n_T b/V, \quad b = \sum_{i=1}^{m} x_i b_i \ , \quad b_i = (\pi/6) N_{Av} \sigma_i^3$$

Equation of State	$\Delta A^{rep}/(n_T RT)$
original van der Waals	$- \ln(1 - 4\xi)$
Mansoori et al.	$- 1.5 \ [1 - \eta_{(1)} + \eta_{(2)} + \eta_{(3)}]$ $+ \ [3\eta_{(2)} + 2\eta_{(3)}]/(1-\xi)$ $+ 1.5 \ [1 - \eta_{(1)} - \eta_{(2)} - \eta_{(3)}/3]/(1-\xi)^2$ $+ (\eta_{(3)} - 1) \ \ln(1-\xi)$ $\eta_{(1)} = \sum_{j>i}^{m} \sum^{m} \Delta_{ij} \ (\sigma_i + \sigma_j)/\sqrt{\sigma_i \sigma_j}$ $\eta_{(2)} = \sum_{j>i}^{m} \sum^{m} \Delta_{ij} \sum_{i=1}^{m} [\sqrt{\sigma_i \sigma_j}/\sigma_1] \ (\xi_1/\xi)$ $\eta_{(3)} = \{ \sum_{i=1}^{m} (\xi_1/\xi)^{2/3} \ x_i^{1/3} \}^3$ $\Delta_{ij} = [(\sigma_i - \sigma_j)^2/\sigma_i \sigma_j] \ \sqrt{x_i x_j} \ \sqrt{\xi_i \xi_j}/\xi$

Table 3a

PURE COMPONENT PARAMETERS* $a = \alpha - \beta T$ and $b = \gamma - \delta T$

Fluid	α bar l^2 mol^{-2}	β 10^{-3} bar l^2 mol^{-2} K^{-1}	γ 10^{-3} l mol^{-1}	δ 10^{-6} l mol^{-1} K^{-1}
CH_4	3.13	2.9	17.77	15.8
C_3H_8	14.13	10.1	36.67	18.0
$n-C_6H_{14}$	43.42	36.5	71.46	37.1
$n-C_7H_{16}$	54.47	42.6	79.73	31.1
$n-C_8H_{18}$	63.46	44.4	82.97	19.2
cyclo-C_6H_{12}	37.90	28.9	60.86	31.6
C_6H_6	31.15	21.6	49.35	22.7
C_6H_5OH	48.59	34.4	50.46	14.6
C_5H_5N	33.37	21.6	45.43	15.7
H_2O	8.23	5.1	10.49	4.2
CH_3OH	16.86	17.1	23.88	15.1

* These parameters were obtained primarily from high-density data. As a result, predicted second virial coefficients tend to be too positive, especially at low temperatures.

Table 3b

GOODNESS OF FIT FOR PURE COMPONENTS IN TABLE 3a

Fluid	T-range / K	Root-mean-square Deviation / Percent	
		saturation pressure	liquid volume
CH_4	92 - 600	2.2	3.6
C_3H_8	250 - 500	6.1*	5.4*
$n-C_6H_{14}$	273 - 507	1.0	1.0
$n-C_7H_{16}$	273 - 537	1.3	1.9
$n-C_8H_{18}$	473 - 553	0.3	0.8
$cyclo-C_6H_{12}$	283 - 353	0.03	0.2
C_6H_6	295 - 460	0.6	0.2
C_6H_5OH	323 - 673	4.3	4.1
C_5H_5N	273 - 389	0.6	0.4
H_2O	293 - 603	0.7	2.0
CH_3OH	293 - 493	0.2	0.3

* These deviations are somewhat higher than expected because strong weight was given to data in the supercritical region. If fitting had been restricted to temperatures below the critical, deviations would be much smaller.

Table 4

BINARY PARAMETERS k_{12}, $\tilde{c}_{12}$ AND $\tilde{c}_{21}$ FOR AQUEOUS LLE USING EQ.(12).

Here $\tilde{c}_{12}=c_{1(2)}/a_{11}^2(T_{c_1})$ and $\tilde{c}_{21}=c_{2(1)}/a_{22}^2(T_{c_2})$ where (2) refers to water.

(T_{c_i} = critical temperature of component i)

(a)

Organic Fluid	k_{12}	$\tilde{c}_{12}$	$\tilde{c}_{21}$
C_3H_8	0.279	-0.033	0.075
$n-C_6H_{14}$	0.235	-0.017	0.121
$n-C_7H_{16}$	0.174	-0.012	0.121
$n-C_8H_{18}$	0.134	-0.020	0.112
$cyclo-C_6H_{12}$	0.289	-0.013	0.113
C_6H_6	0.161	-0.006	0.067
C_6H_5OH	-0.021	0.008	0.024
C_5H_5N	0.062	0.013	0.052

(b) Methane-Water

T / K	k_{12}	$\tilde{c}_{12}$	$\tilde{c}_{21}$
311	0.328	-0.048	0.041
378	0.339	-0.038	0.039
423	0.314	-0.032	0.034
473	0.239	-0.149	0.024
523	0.187	-0.220	0.014

Table 5

SECOND VIRIAL CROSS COEFFICIENT B_{12}

$$-B_{12} \; / \; cm^3 \; mol^{-1}$$

	T / K	experimental	calculated[‡]
n-hexane - water	360	189†	250
	400	150†	204
	440	121†	167
n-heptane - water	373	206*	299
	398	185*	266
	423	170*	235
methane - water	311	55†	56
	378	31†	34
	423	24†	27

† Wormald (1982)

* Richards et al. (1981)

[‡] Equation (4) using k_{12} from LLE data

Table 6

BINARY PARAMETERS FROM VLE CORRELATION[*]

Binary System	k_{12}	$\tilde{c}_{12}$	$\tilde{c}_{21}$
methanol(1)-benzene(2)	-0.502	-0.133	-0.066
methanol(1)-water(2)	0.000	0.006	0.008
pyridine(1)-water(2)	0.062	0.013	0.052
benzene(1)-pyridine(2)	0.123	0.022	0.019

[*] $\tilde{c}_{12}$ and $\tilde{c}_{21}$ as defined in Table 4

Table 7

LIQUID-LIQUID MISCIBILITY LIMITS PREDICTED BY THE EOS FOR 1.013 bar and 25° C

	Miscibility Gap	
	from	to
pyridine(1)-water(2)	$x_1 = 0.036$	$x_1 = 0.100$
methanol(1)-benzene(2)	$x_1 = 0.188$	$x_1 = 0.314$

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FIGURE CAPTIONS

Fig. 1   Liquid-liquid equilibria for benzene(1)-water(2) at three-phase (LLV)
         saturation pressure (experimental: Tsonopoulos and Wilson, 1983)

Fig. 2   Liquid-liquid equilibria for cyclohexane(1)-water(2) at three-phase
         (LLV) saturation pressure (experimental: Tsonopoulos and Wilson, 1983)

Fig. 3   Liquid-liquid equilibria for n-hexane(1)-water(2) at three-phase (LLV)
         saturation pressure (experimental: Tsonopoulos and Wilson, 1983)

Fig. 4   Liquid-liquid equilibria for n-heptane(1)-water(2) at 1 bar
         (experimental: quoted in Sorensen and Arlt, 1979)

Fig. 5   Liquid-liquid equilibria for n-octane(1)-water(2) at three-phase (LLV)
         saturation pressure (experimental: GPA, 1982)

Fig. 6   Liquid-liquid equilibria for phenol(1)-water(2) at 1 bar
         (experimental: quoted in Sorensen and Arlt, 1979)

Fig. 7a Phase diagram for propane(1)-water(2) at 344.26 K
    7b   Liquid-liquid equilibria for propane(1)-water(2) at 103.4 bar
    7c   Vapor-liquid equilibria for propane(1)-water(2) at 6.89 bar
         (experimental: Kobayashi and Katz, 1953)

Fig. 8a Saturated-liquid compositions in methane(1)-water(2)
         (experimental: 311-378 K: Culberson and McKetta, 1951; 423-523 K:
         Sultanov et al., 1972)
    8b   Saturated-vapor compositions in methane(1)-water(2)
         (experimental: 311-378 K: Olds et al., 1942; 423-523 K: Sultanov
         et al., 1971)

SYMBOLS

A Helmholtz energy
a van der Waals attractive parameter
$\underline{a}$ molar Helmholtz energy
$\overline{B}$ second virial coefficient
b van der Waals size parameter
c, k binary parameters
m number of components
n_T total number of moles
N_{Av} Avogadro's number
R gas constant
T temperature
V total volume
x mole fraction
α, β coefficients for temperature dependence of a
γ, δ coefficients for temperature dependence of b
σ molecular size parameter
ρ molar density
Θ algebraic function of reduced density for attractive part of Helmholtz energy
ξ reduced density

Superscripts

o standard state (temperature T, pure ideal gas at 1 bar)
EOS equation of state
H Helmholtz energy
c central
nc noncentral
rep repulsive

Subscripts

i component
c critical
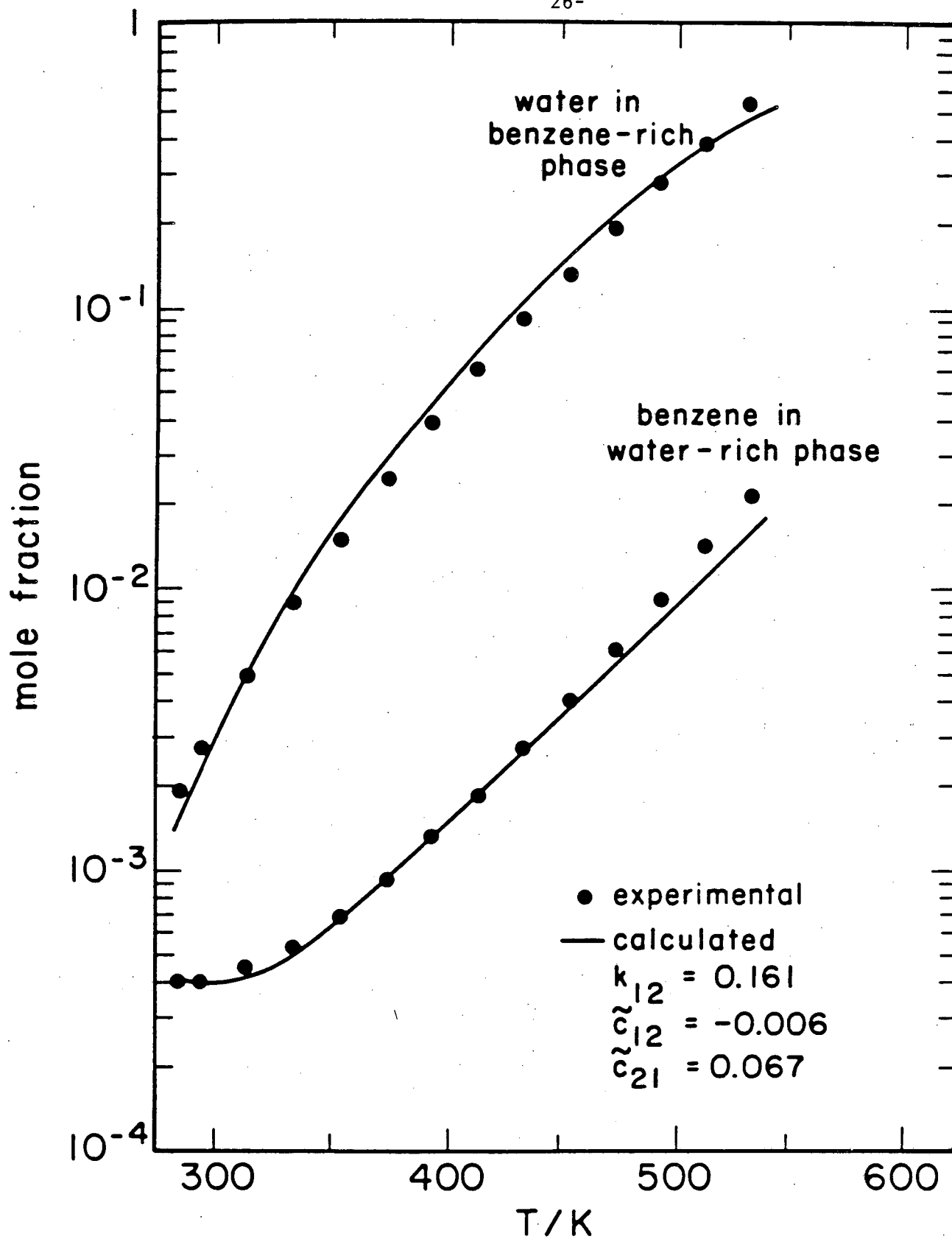
Fig. 1 <u>Liquid-Liquid Equilibria for Benzene (1)-Water (2) at Three-Phase (LLV) Saturation Pressure</u>
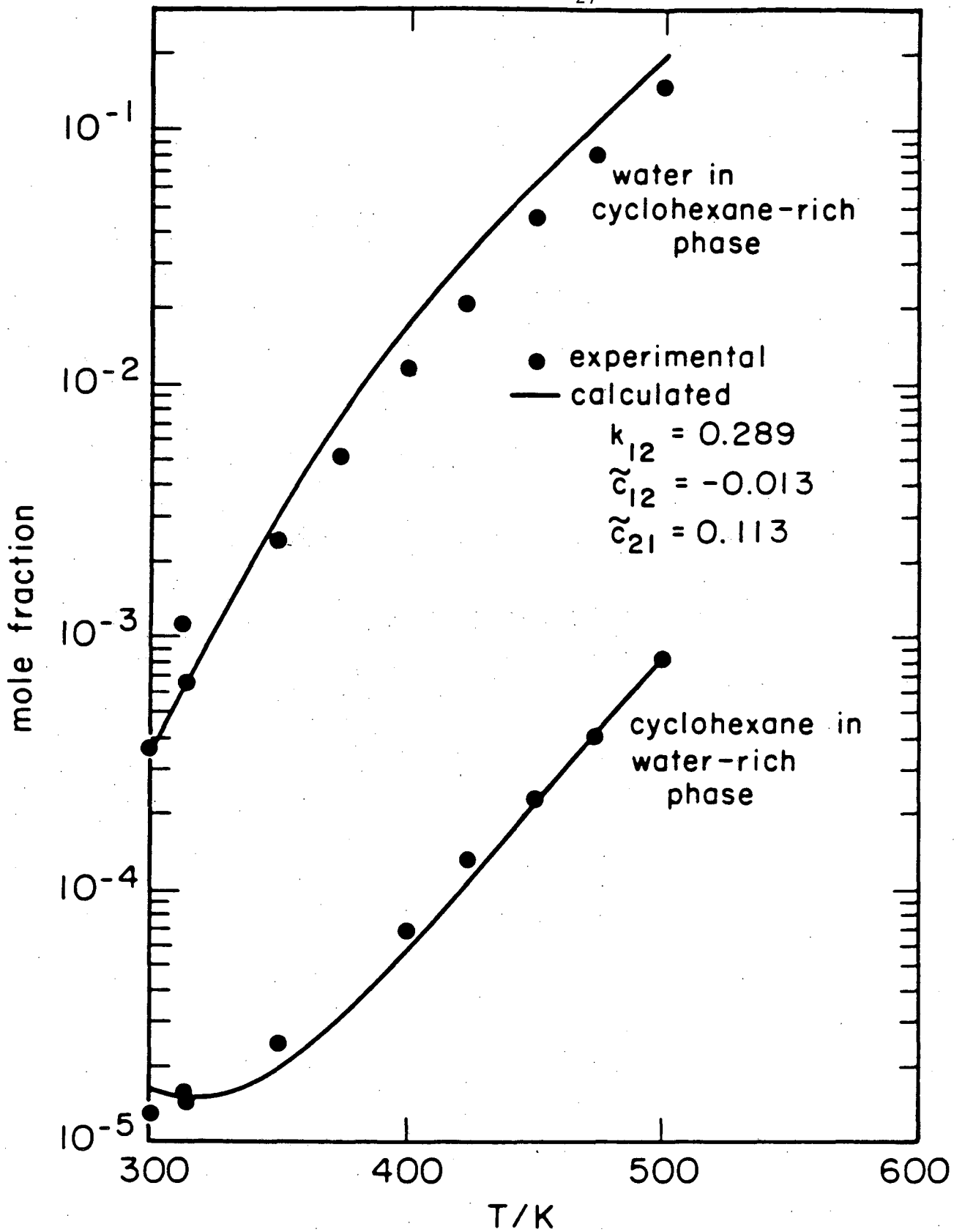
Fig. 2 Liquid-Liquid Equilibria for Cyclohexane (1)-
Water (2) at Three-Phase (LLV) Saturation
Pressure
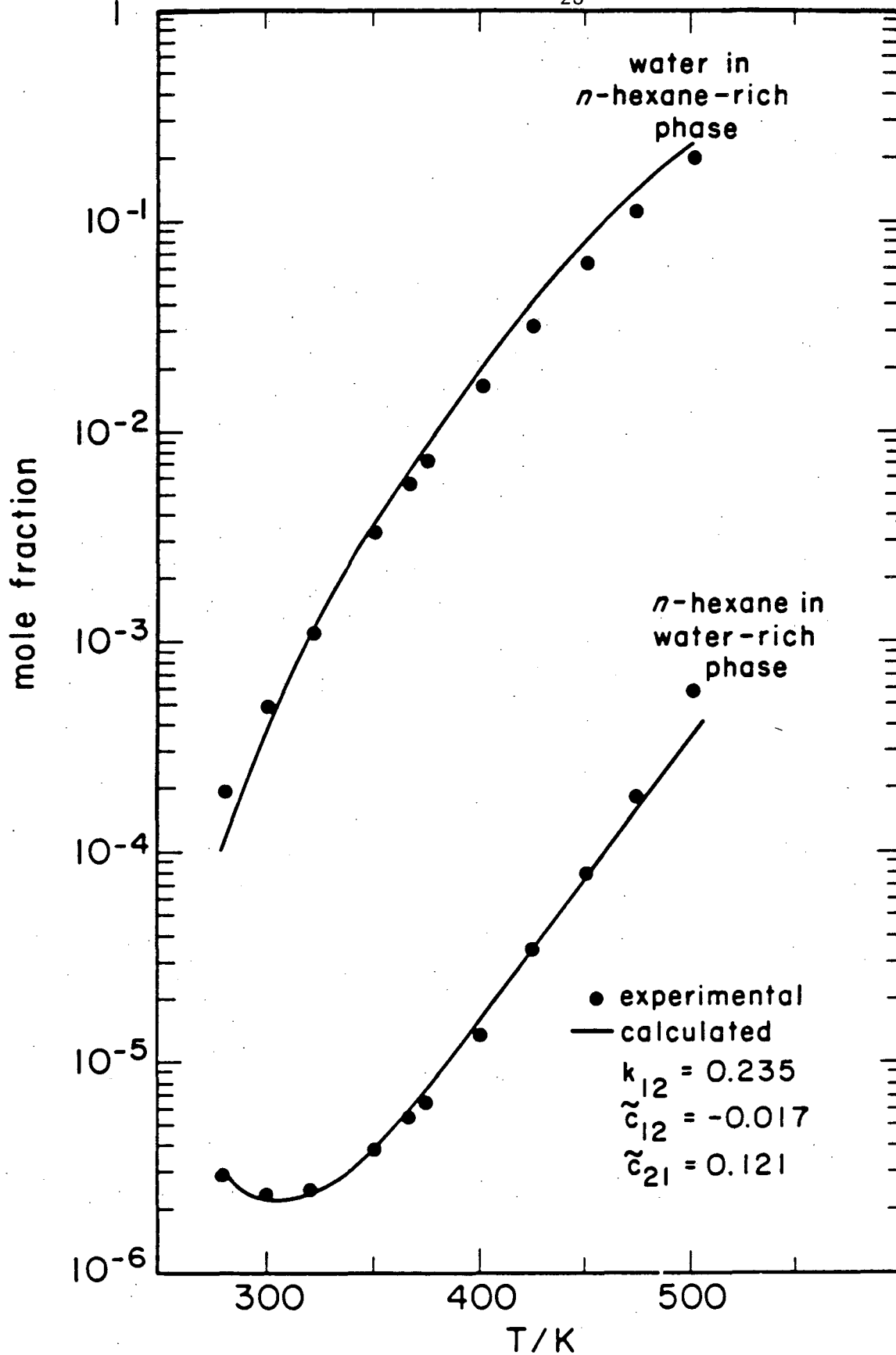
Fig. 3 Liquid-Liquid Equilibria for *n*-Hexane (1)-Water (2) at Three-Phase (LLV) Saturation Pressure
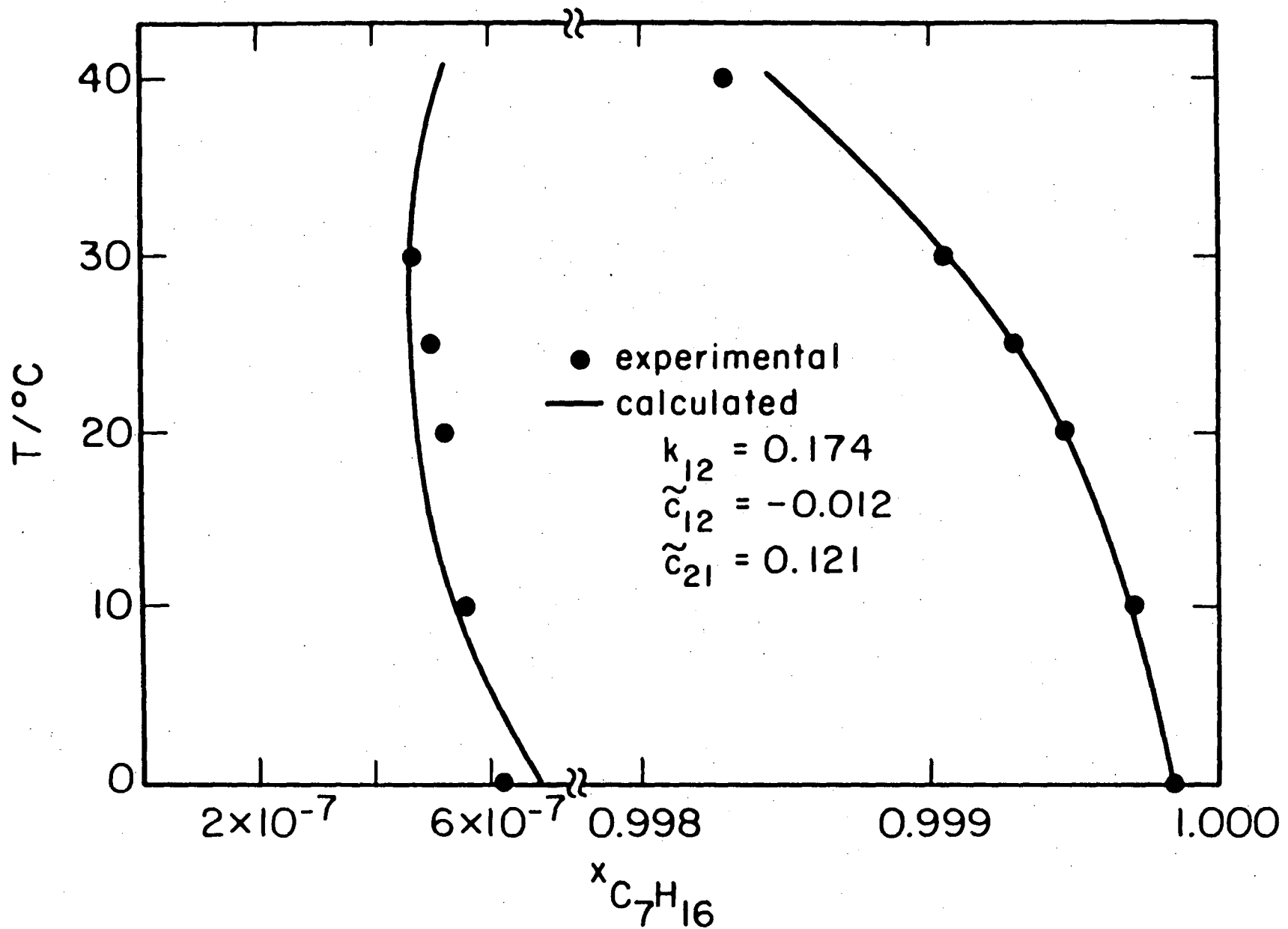
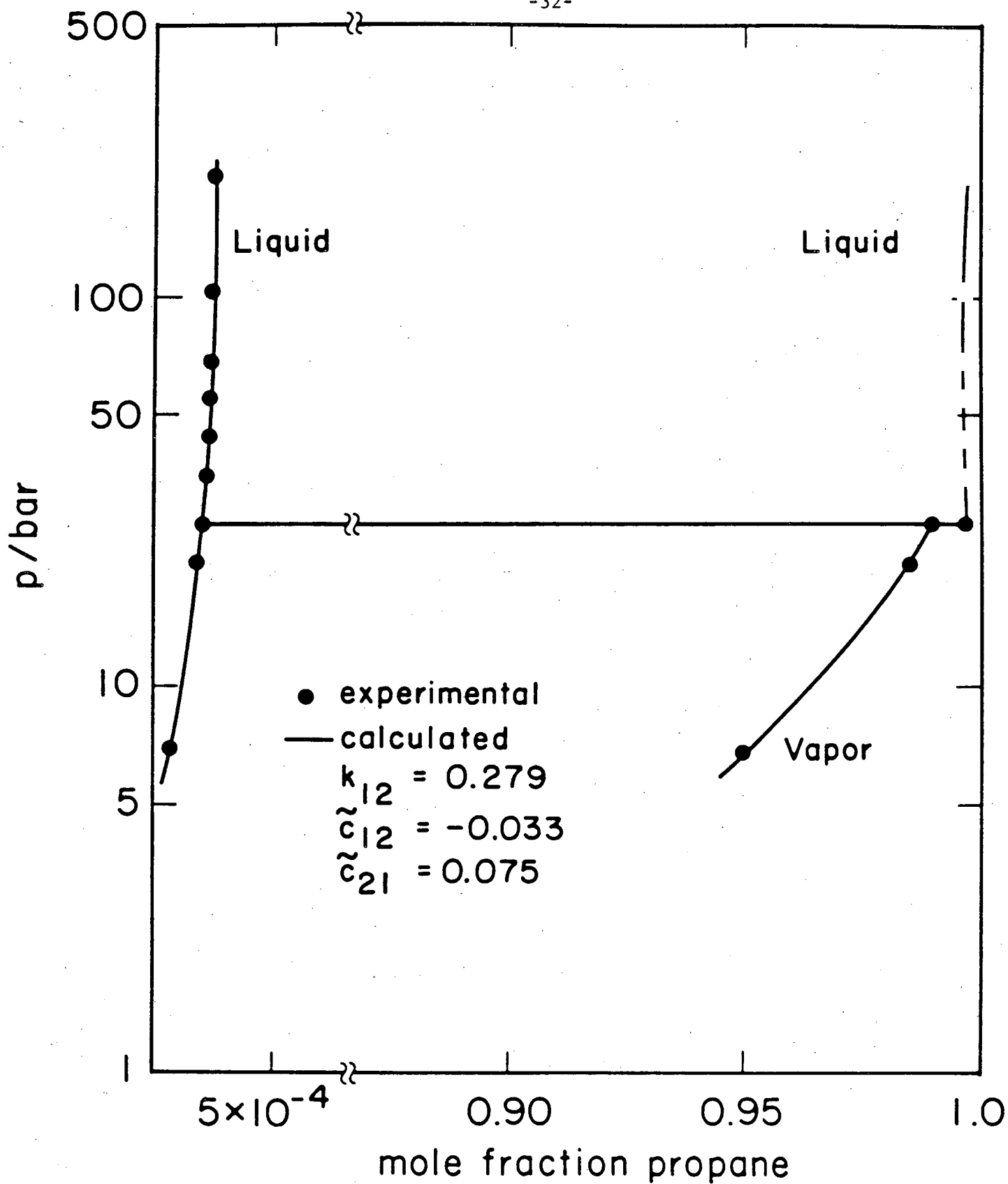Fig. 4   Liquid–Liquid Equilibria for *n*-Heptane (1)–Water (2) at 1 bar
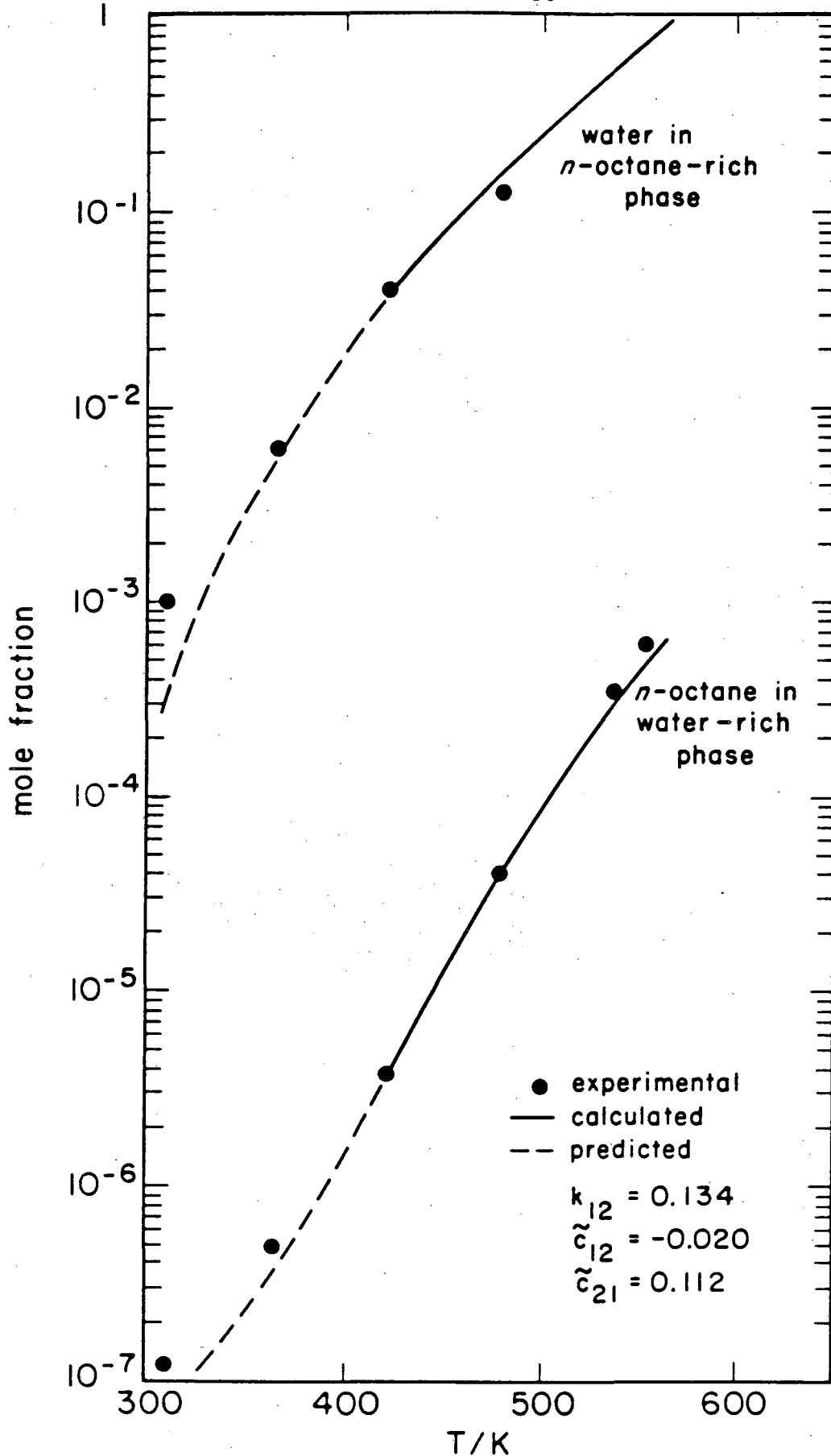
Fig. 5 Liquid-Liquid Equilibria for *n*-Octane (1)-Water (2) at Three-Phase (LLV) Saturation Pressure
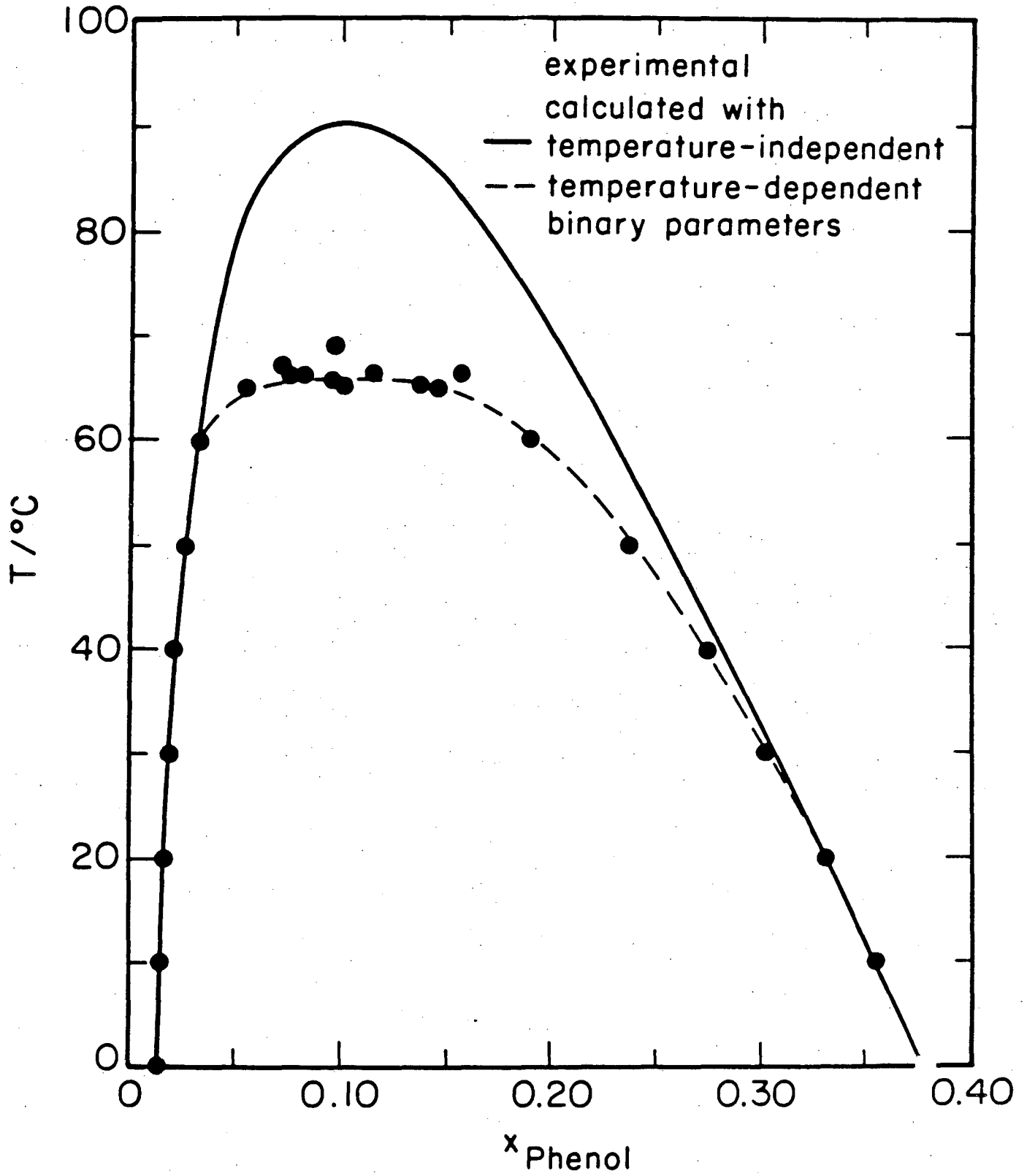
Fig.6 Liquid-Liquid Equilibria for Phenol (1) − Water (2) at 1 bar

Fig. 7a Phase Diagram for Propane (1) – Water (2) at 344.26 K
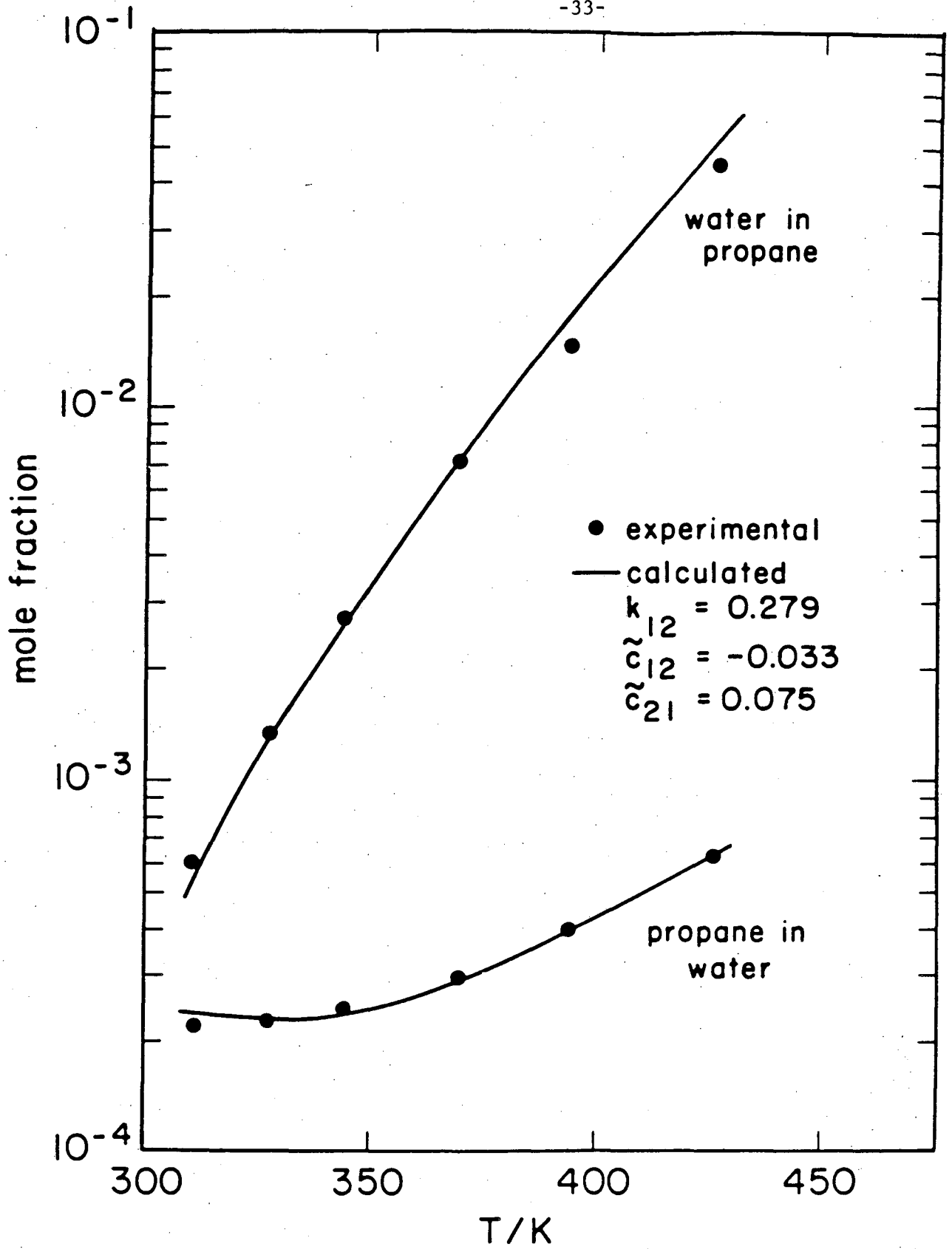
Fig. 7b Liquid-Liquid Equilibria for Propane (1) - Water (2) at 103.4 bar
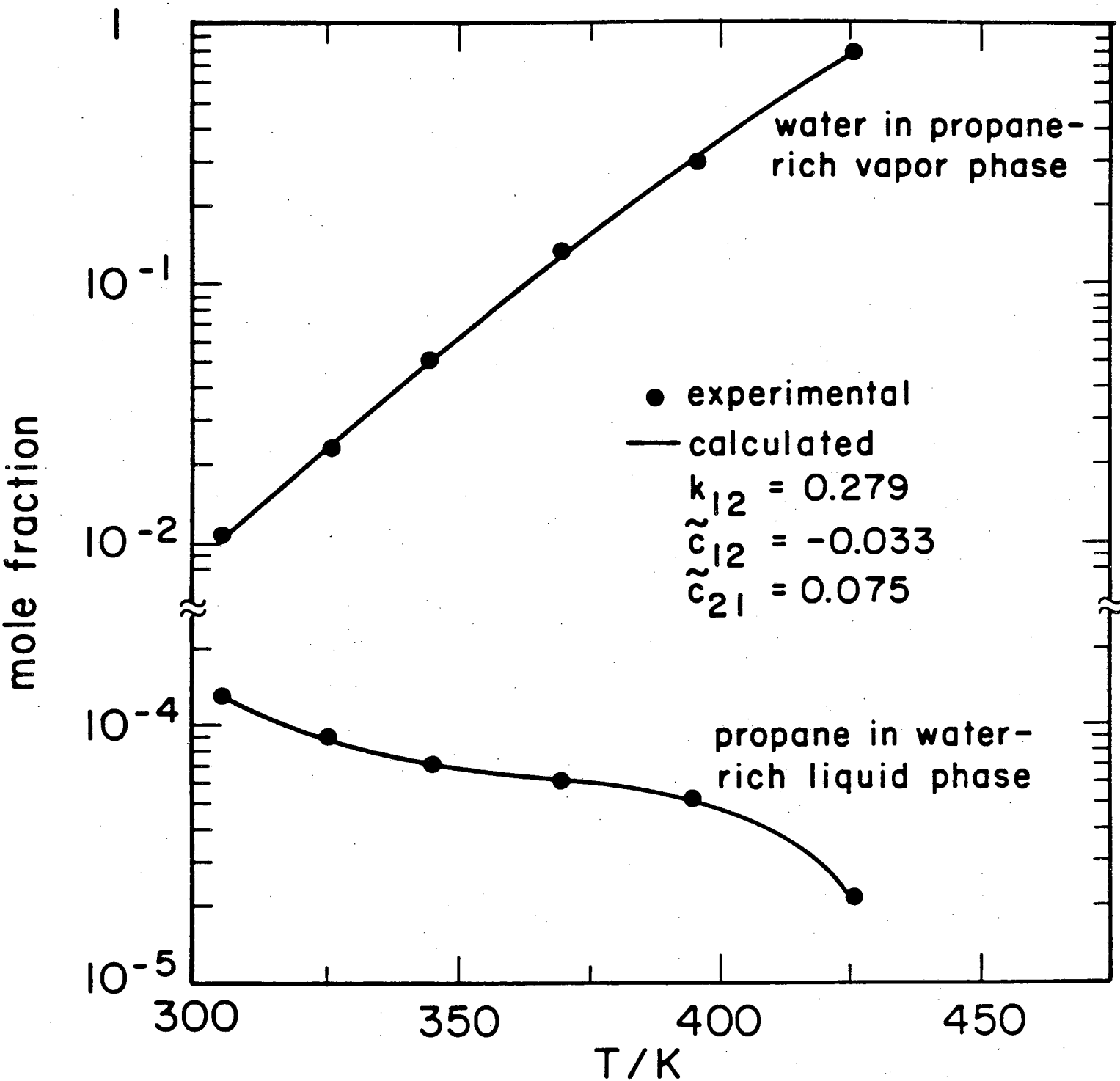
Fig. 7c **Vapor-Liquid Equilibria for Propane (1) - Water (2) at 6.89 bar**
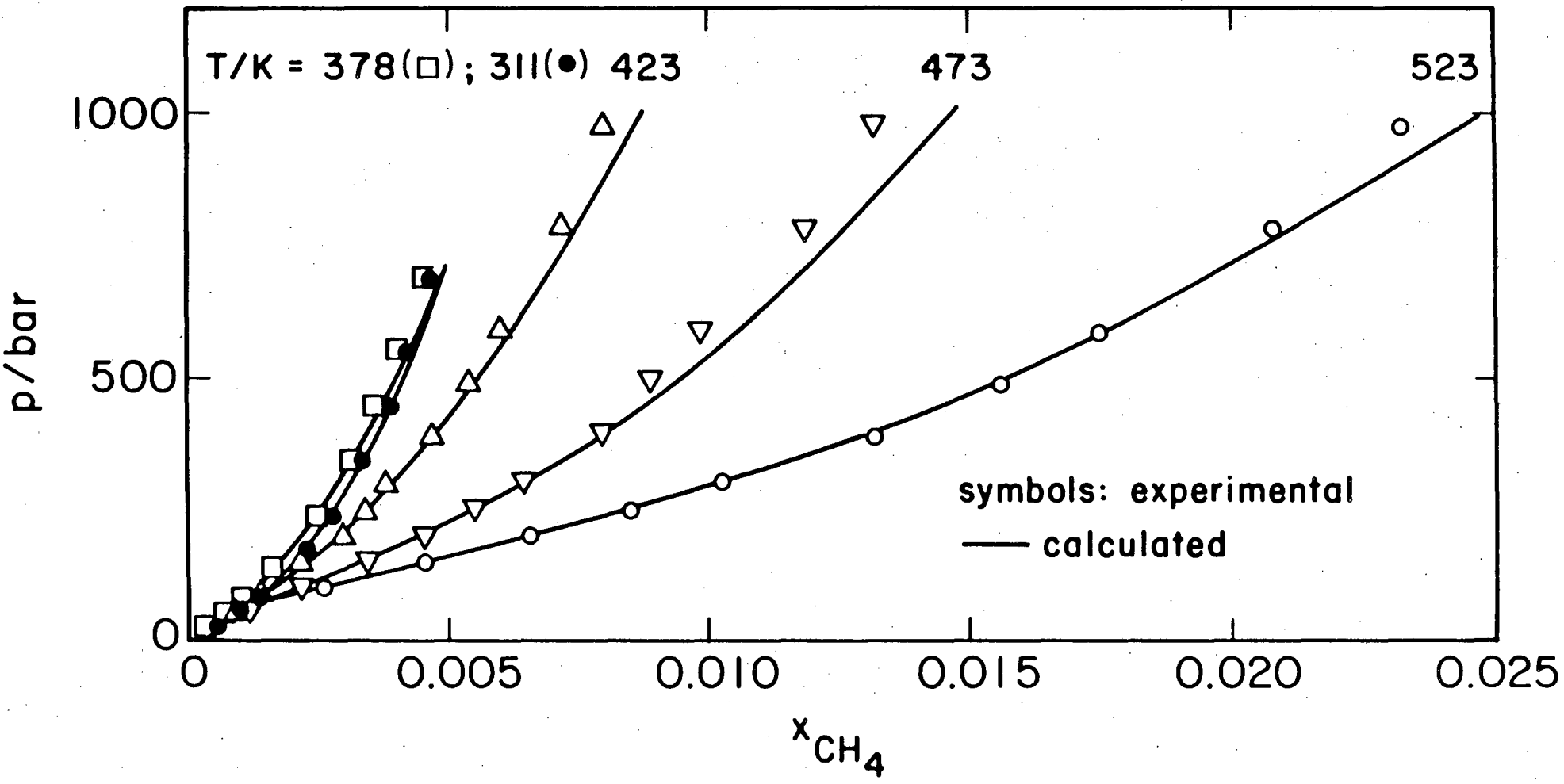
Fig. 8a   Saturated-Liquid Compositions in Methane (1) - Water (2)

Fig. 8b Saturated-Vapor Compositions in Methane (1) – Water (2)