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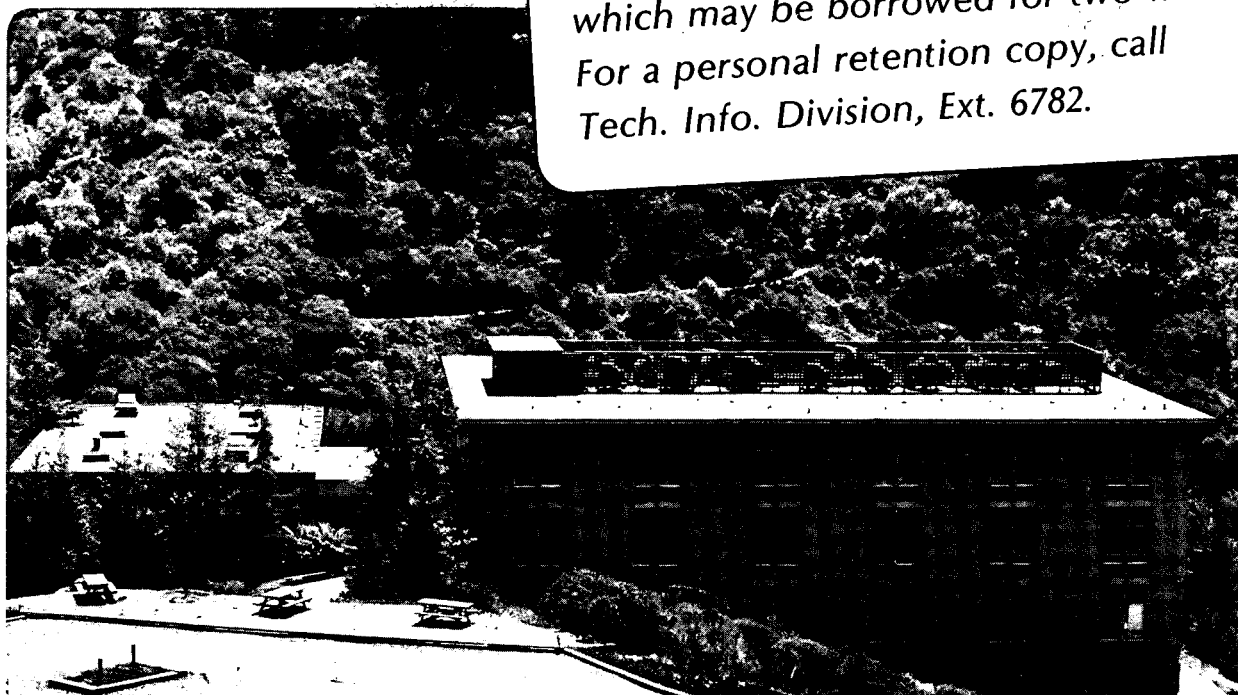
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A Thermodynamic Method for Simultaneous
Representation of Ternary Vapor-Liquid
and Liquid-Liquid Equilibria

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Abstract

When common expressions for the excess Gibbs energy g^E are used to predict ternary phase equilibria on the basis of binary data alone, calculated vapor-liquid equilibria (VLE) are generally satisfactory but calculated liquid-liquid equilibria (LLE) are often poor. This work proposes that the usual ternary expression for g^E be multiplied by a composition-dependent correction factor C such that $C=1$ whenever the ternary degenerates to a binary. Correction factor C is always near unity and therefore has little effect on ternary VLE; however, its effect on LLE is large. Illustrative results are given for 19 ternary systems. When reliable binary VLE data and reliable ternary LLE data are available, the method proposed here gives a good thermodynamic representation of ternary VLLE suitable for computer-aided design of separation processes.

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While chemical-engineering thermodynamicists have given much attention to ternary vapor-liquid equilibria (VLE) and to ternary liquid-liquid equilibria (LLE), little attention has been given toward simultaneous representation of both vapor-liquid and liquid-liquid equilibria for a ternary system. Such representation, however, is necessary for design of separation operations (e.g. extractive or azeotropic distillation) where, for at least part of the operation, there exist two liquid phases in addition to a vapor phase (Treybal, 1963). Gaube and coworkers (Fuchs et al., 1983) recently suggested an approximate procedure for calculating ternary VLLE with special application to the system Acetonitrile-n-Heptane-Benzene. We propose here an alternate procedure which, in contrast to that of Gaube, does not suffer from thermodynamic inconsistency.

Our procedure is intended for a three-component mixture of nonelectrolyte fluids where one of the constituent binaries may exhibit a miscibility gap. (A ternary system with two pairs completely miscible and one pair partially miscible is often called a Type I system.) We confine attention to systems at moderate pressures, well removed from vapor-liquid critical conditions. For such systems, vapor-phase properties are described by the virial equation of state (truncated after the second term) or by a "chemical" theory of vapor-imperfections due to dimer formation as discussed elsewhere. (See, for example, Prausnitz, 1980.) For liquid-phase properties, we use activity coefficients as represented

by an excess-Gibbs-energy function. Our representation requires experimental VLE data for the two completely miscible binaries and LLE data for the ternary.

Thermodynamic Framework

One of the main advantages of the excess-Gibbs-energy concept is that it provides a convenient framework for calculating ternary phase equilibria using only experimental data for the three constituent binaries, as discussed in numerous texts. (See, for example, Prausnitz, 1969.) At constant temperature, we can extend to three components some binary expression (e.g. NRTL or UNIQUAC) giving molar excess Gibbs energy g^E as a function of mole fraction x . Subject to some simplifying assumptions, we then have g^E for the ternary as a function of mole fractions, using only coefficients obtained from binary data. In dimensionless form, we designate this function $(g^E/RT)_{123}^0$.

When typical binary VLE data are regressed to fit some expression for g^E , several sets of "optimum" binary parameters can be obtained; only for highly accurate data is it possible to obtain a unique set. When attention is restricted to a binary system, this uncertainty is of little interest but when binary parameters are used to "scale-up" toward prediction of ternary equilibria through $(g^E/RT)_{123}^0$, uncertainties in the binary parameters affect the prediction. Experience has shown that such uncertainties have little effect on calculated ternary VLE but they have a very large effect on calculated ternary LLE for Type I systems. (See,

for example, Schulte et al., 1980.)

When binary data alone are used for Type I systems, the calculated two-phase region is often much larger than that observed. The current state of the art is such that binary data alone are often sufficient to predict ternary VLE with satisfactory accuracy but they are hardly ever sufficient to predict satisfactory Type I ternary LLE. If one wishes to represent such ternary LLE with a model for g^E using only binary parameters, it is necessary to adjust these binary parameters in the light of the ternary LLE data, as shown, for example, by Anderson (1978). However, when that is done, the adjusted binary parameters may introduce some error in the calculated binary VLE.

Our proposal here is to retain the function $(g^E/RT)_{123}^0$ as determined from binary data, but to correct that function slightly, using an empirical correction factor C as determined from ternary LLE data. This correction factor depends on composition but reduces to unity whenever the ternary degenerates to a binary; therefore calculated binary VLE are not affected. This correction factor C is always near unity and therefore has little effect on calculated ternary VLE. But it has a profound effect on calculated ternary LLE.

For a ternary system, we propose that the dimensionless molar excess Gibbs energy is of the form

$$\left(\frac{g^E}{RT}\right)_{123} = C \left(\frac{g^E}{RT}\right)_{123}^0 \quad (1)$$

We obtain $(g^E/RT)_{123}^0$ from experimental VLE data for the two

completely miscible pairs and from mutual-solubility data for the partially miscible pair.

For correction factor C we propose the empirical form

$$C = \exp [\alpha x_1^{\lambda_1} x_2^{\lambda_2} x_3^{\lambda_3}] \quad (2)$$

where x_1 = mole fraction of component 1 (etc.) and α is a constant. Exponents λ_1 , λ_2 and λ_3 are also constants but, to prevent singularities in the activity coefficients, it is necessary that each of these λ 's be equal to or larger than unity.

For convenience, let

$$\lambda_1 = \left(\frac{\bar{x}_1}{x_3}\right)\beta \quad \text{and} \quad \lambda_2 = \left(\frac{\bar{x}_2}{x_3}\right)\beta \quad (3)$$

where $\beta = \lambda_3$.

The mole fractions \bar{x}_1 , \bar{x}_2 and \bar{x}_3 represent the ternary composition where the absolute value of $\ln C$ is a maximum.

Since

$$\bar{x}_1 + \bar{x}_2 + \bar{x}_3 = 1, \quad (4)$$

Equation (2) has four adjustable parameters: α , β , \bar{x}_1 and \bar{x}_2 .

For some ternary systems a reasonable simplification is to assume that

$$\bar{x}_1 = \bar{x}_2 = \bar{x}_3 = 1/3. \quad (5)$$

In that event, Equation (2) simplifies to

$$C = \exp [\alpha (x_1 x_2 x_3)^\beta] \quad (2a)$$

with only two adjustable parameters, α and β . As shown below, Equation (2a) is satisfactory for many ternary

mixtures.

When Equation (2) is substituted into Equation (1), we can derive the activity coefficient γ_i for component i using the standard relation

$$RT \ln \gamma_i = \left(\frac{\partial n_T g^E}{\partial n_i} \right)_{T,P,n_j \dots} \quad (6)$$

where n_i is the number of moles of component i and n_T is the total number of moles. Performing the indicated differentiation, we obtain

$$\ln \gamma_i = C \ln \gamma_i^0 + C \left(\frac{\lambda_i}{x_i} - \lambda_1 - \lambda_2 - \lambda_3 \right) (\ln C) (g^E/RT)_{123}^0 \quad (7)$$

$$\text{where } \ln \gamma_i^0 = \left(\frac{\partial (n_T g^E/RT)_{123}^0}{\partial n_i} \right)_{T,P,n_j \dots} \quad (8)$$

If Equation (2a) is used instead of Equation (2), we obtain

$$\ln \gamma_i = C \ln \gamma_i^0 + C \beta \left(\frac{1}{x_i} - 3 \right) (\ln C) (g^E/RT)_{123}^0 \quad (7a)$$

Application of the Proposed Method

Equation (1) was applied to 19 ternary systems identified in Table 1. For 16 of these ternaries, binary data were used to obtain UNIQUAC parameters; these are given in Table 2A. For the remaining 3 ternaries, binary data were used to obtain NRTL parameters; these are given in Table 2B. Data sources are given in Appendix I. The binary parameters are used to find $(g^E/RT)_{123}^0$.

For 7 ternaries, Equation (2a) was used for correction function C; parameters α and β are given in Table 3A. For the remaining 12 ternaries, Equation (2) was used for correction function C; parameters α , β , \bar{x}_1 and \bar{x}_2 are given in Table 3B. Appendix II presents a brief summary of the calculation procedure used to obtain ternary parameters.

Figure 1 shows calculated and experimental results for three ternary systems where the binodal curve shows only modest asymmetry. In each case, calculated results, using binary data alone, give poor ternary LLE. When correction function C is used in the calculation, ternary LLE are improved dramatically. Figure 2 shows similar results for three other ternary systems where the binodal curve is strongly asymmetric.

In our calculations, Equation (2a) was used when the ternary binodal line was reasonably symmetric and when the binary data provided a fair first approximation for the ternary LLE. Otherwise Equation (2) was used.

Figure 3 shows calculated selectivities for two ternary systems. When correction function C is included in the calculations, the results are very much better.

The top part of Figure 4 shows calculated ternary LLE for System XIII at 45°C. To predict ternary LLE at 25°C, we used the same ternary parameters and the same binary parameters for the two miscible pairs. We changed only the binary parameters for the partially miscible pair. Predicted and observed results are shown at the bottom of Figure 4.

Binary Parameters

Because the proposed model relies on the uncorrected model to give a first approximation, it is important to select binary parameters carefully; it is particularly important to use binary data which were obtained at a temperature close to that of the ternary system.

The binary parameters for the partially miscible pair are generated from mutual-solubility data at system temperature. Hence, accuracy of the mutual solubilities is very important. Magnussen et al. (1980) pointed out that in a ternary, the calculated distribution ratio may be in serious error when there is appreciable uncertainty in the binary mutual solubilities. This error is more likely to be serious when the mutual solubilities are very low. Small adjustments in the binary mutual solubilities may produce large improvement in the ternary diagram.

If the uncorrected model gives very poor prediction of the ternary phase diagram, the proposed correction may provide some improvement but it may be insufficient for satisfactory quantitative agreement with experiment. In other words, the binary parameters alone must provide at least a rough first approximation; our correction function is no more than what is implied by those words: it does not create a ternary diagram but only corrects it.

Ternary LLE and VLE

As noted by previous authors (Fuchs et al., 1983), calculated ternary LLE are sensitive to small changes in the molar excess Gibbs energy g^E . When a model for g^E uses only binary parameters, calculated ternary LLE are sensitive to small changes in the binary parameters. Since prediction of binary VLE data usually cannot give unique binary parameters, and since g^E models provide only approximations, it is not possible at present to predict ternary LLE from binary data alone; our experience is that in some fortuitous cases binary data alone are sufficient but in many other cases they are not.

As shown by Anderson (1978), it is often possible to represent ternary LLE well with a g^E model that contains only binary parameters provided that these parameters are obtained from ternary LLE and binary data. However, in that event, if the ternary LLE data are reproduced with good accuracy, the binary VLE data are often reproduced with only fair accuracy. By contrast, the procedure presented here allows simultaneous representation of ternary LLE and binary VLE with good accuracy.

Since ternary LLE are sensitive to activity coefficients, but independent of pure-component vapor pressures, correction function C need not be large; indeed, it is never far removed from unity. For the systems studied here, the required correction to $(g^E/RT)_{123}^0$ is usually a few percent and only rarely more than (about) ten percent. Table 4

presents typical values of C . While these small corrections have a large effect on ternary LLE, they have only a minor effect on ternary VLE where accurate pure-component vapor pressures are more important than accurate activity coefficients.

While we could not make an extensive study of the effect of C on ternary VLE, we investigated ternary VLE for System I (Table 5) where reliable ternary VLE data are available. For this system, correction function C has essentially no effect on ternary VLE. The magnitude of C , as shown in Table 4, suggests that, for a given ternary system, inclusion of C in phase-equilibrium calculations provides large improvement in calculated LLE but very small change in calculated VLE. The method presented here, therefore, may be useful for design of separation processes such as extractive or azeotropic distillation where part of the process is concerned with one liquid phase and another with two liquid phases.

Acknowledgment

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Table 1.

Ternary Systems Studied

	(1)	(2)	(3)
I	acetonitrile	n-heptane	benzene
II	methanol	n-heptane	benzene
III	methanol	cyclohexane	ethanol
IV	acetonitrile	cyclohexane	ethanol
V	acetonitrile	cyclohexane	toluene
VI	n-hexane	sulfolane	benzene
VII	water	ethyl acetate	methanol
VIII	water	ethyl acetate	ethanol
IX	water	nitroethane	n-propanol
X	water	chloroform	acetone
XI	furfural	2,2,4-trimethylpentane	benzene
XII	cyclohexane	furfural	benzene
XIII	acetonitrile	cyclohexane	benzene
XIV	cyclohexane	nitromethane	benzene
XV	cyclohexane	sulfolane	benzene
XVI	water	acrylonitrile	acetonitrile
XVII	n-heptane	n-methylpyrrolidone	benzene
XVIII	n-hexane	acetonitrile	ethanol
XIX	cyclohexane	sulfolane	benzene

Table 2A.

Binary Parameters in UNIQUAC Equation, K
(Temperature, K)

System	a_{12}	a_{21}	a_{13}	a_{31}	a_{23}	a_{32}
I	17.4 (318)	571.4	-51.54 (318)	247.13	31.35 (318)	19.07
II	2.49 (305.8)	1419.32	-56.05 (308)	988.6	31.35 (318)	19.07
III	15.91 (298)	1518.2	344.9 (298)	-193.12	1458.38 (308)	-89.26
VI	35.337 (313)	554.36	430.51 (293)	68.72	1349.2 (278)	-68.0
V	36.06 (318)	541.0	-162.58 (318)	414.41	252.9 (323)	-184.71
VI	541.394 (373)	44.031	28.8274 (373)	-1.9879	30.2164 (373)	136.87
VII	28.366 (293)	710.0	433.98 (373)	-221.91	579.61 (335-347)	-107.54
VIII	28.366 (293)	710.0	284.81 (313)	-27.38	594.6 (313)	-148.29
IX	138.44 (298)	920.08	587.18 (333)	23.26	574.22 (368)	-94.39
X	396.84 (298)	548.17	-128.35 (298)	636.17	28.38 (308)	-140.77
XI	-4.98 (298)	410.08	192.72 (355-427)	-85.0	91.65 (353-368)	-35.12
XII	354.83 (298)	41.17	70.13 (313)	-11.2	192.72 (355-427)	-85.0
XIII	36.06 (318)	541.0	-47.5 (318)	241.78	95.67 (318)	-37.06
XIV	529.19 (298)	95.01	70.13 (313)	-11.2	29.71 (298)	134.43
XV	443.23 (373)	84.665	106.96 (373)	-57.247	30.216 (373)	136.87
XVI	155.78 (333)	471.21	61.92 (350-364)	294.1	80.53 (351-354)	-49.84

Table 2B

Binary Parameters in NRTL Equation*

(Temperature, K)

System	g_{12}	g_{21}	α_{12}	g_{13}	g_{31}	α_{13}	g_{23}	g_{32}	α_{23}
XVII	1207.87 (298)	1076.65	0.363	-155.98 (298)	627.78	0.4	-405.44 (298)	701.56	0.455
XVIII	966. (313)	1107.75	0.2	1662.22 (313)	949.4	0.47	342.16 (313)	547.5	0.3
XIX	2473.99 (373)	802.31	0.2	90.96 (373)	110.67	0.3	58.75 (373)	908.99	0.3

* g_{ij} is in calories/mole.

Table 3A

Parameters for Correction Function C (Equation 2a)

System	Temp., K	α	β
XI	298	2.403	1.0
XII	298	0.9438	1.0
XIII	318	-2.346	1.0
XIV	298	-1.818	1.0
XV	373	-2.000	1.02
XVI	333	-2.750	1.40
XIX	373	-1.728	1.0

Table 3B
Parameters for Correction Function C (Equation 2)

System	Temp., K	α	β	\bar{x}_1	\bar{x}_2
I	318	-3.857	1.000	0.4413	0.2944
II	305.8	-2.857	1.000	0.6199	0.2272
III	298	-0.5165	1.102	0.2921	0.3859
IV	313	-2.419	1.025	0.2762	0.4406
V	318	-12.60	1.894	0.2071	0.4006
VI	373	-813.6	3.224	0.08731	0.6312
VII	293	-1.817	1.767	0.2801	0.2602
VIII	293	-3.535	1.227	0.3753	0.2806
IX	298	-5.362	1.172	0.4096	0.2825
X	298	118.4	1.706	0.5440	0.1685
XVII	298	-2.841	1.337	0.4334	0.2425
XVIII	313	-2.902	1.397	0.4359	0.2353

Table 4
Typical Values of C in Ternary Systems

System	x_1	x_3	C	Region
I	0.5	0.1	0.9573	p
	0.45	0.15	0.9466	p
	0.3	0.5	0.9579	m
	0.1	0.8	0.9949	m
III	0.6	0.05	0.9972	p
	0.45	0.1	0.9936	p
	0.3	0.2	0.9895	m
	0.2	0.5	0.9902	m
XVI	0.5	0.1	0.9886	p
	0.45	0.15	0.9826	p
	0.3	0.3	0.9742	m
	0.1	0.5	0.9886	m
XI	0.5	0.1	1.049	p
	0.4	0.3	1.090	p
	0.3	0.5	1.075	m
	0.2	0.7	1.034	m

p = partially miscible (two-phase) region

m = miscible (one-phase) region

Table 5.

Comparison of VLE between uncorrected model (a)
and corrected model (b) for a ternary system
at 45°C:
Acetonitrile(1)-n-Heptane(2)-Benzene(3)

x_1	x_2		y_1	y_2	P, atm
0.0297	0.1055	measured	0.087	0.076	0.312
		calc (a)	0.083	0.087	0.309
		calc (b)	0.083	0.087	0.309
0.4733	0.0130		0.469	0.026	0.373
			0.466	0.027	0.372
			0.467	0.024	0.371
0.1345	0.1725		0.286	0.128	0.366
			0.289	0.127	0.355
			0.280	0.127	0.352
0.2958	0.5162		0.580	0.275	0.416
			0.605	0.258	0.432
			0.581	0.279	0.409
0.3790	0.3896		0.561	0.260	0.417
			0.572	0.253	0.423
			0.558	0.264	0.440
0.4282	0.3595		0.568	0.264	0.418
			0.574	0.263	0.423
			0.569	0.268	0.406

Appendix I
References for 19 Systems

System	References
I	Palmer (1972), Prausnitz (1980)
II	Wittrig (1977), Prausnitz (1980)
III	Nagata (1983)
IV	Nagata (1980), Prausnitz (1980)
V	Nagata (1983)
VI	Mukhopadhyay (1982)
VII	Beech (1938), Prausnitz (1980)
VIII	Beech (1938), Prausnitz (1980)
IX	Malone (1967), Prausnitz (1980)
X	Hand (1930), Prausnitz (1980)
XI	Henty (1964), Prausnitz (1980)
XII	Henty (1964), Prausnitz (1980)
XIII	Nagata (1983)
XIV	Weck (1954), Prausnitz (1980)
XV	Mukhopadhyay (1982)
XVI	Volpicelli (1968), Prausnitz (1980)
XVII	Fabries (1977)
XVIII	Sugi (1978)
XIX	Mukhopadhyay (1982)

Appendix II
Calculation Procedure Used to Obtain
Ternary Parameters

The calculations can be conveniently represented by three steps:

(i) Calculate ternary LLE with uncorrected model using the method discussed by Sørensen et al. (1979). If the calculated partially miscible region is larger than that indicated by the experimental data, α is negative and vice versa.

(ii) Using the "simplex" method (a function comparison method; Nelder and Mead, 1965), find the best α and β ($\beta \geq 1$) with Equation 7a. (This calculation uses Equation 5.) A typical value of β is 1.0. If the prediction is not satisfactory, Equation 7 should be used as indicated in Step (iii).

(iii) By comparing the shape of the calculated binodal curve with that obtained from experiment, move (\bar{x}_1, \bar{x}_2) from $(\frac{1}{3}, \frac{1}{3})$ toward a new position where a larger correction is needed. Then, using the "simplex" method, find the best four parameters with Equation 7 ($\lambda_1, \lambda_2, \lambda_3 \geq 1$). Several different initial estimate combinations should be tried to find the "best" parameters. Typical values for λ 's are between 1 and 2, but in some cases a particular λ may be as large as 7.

To perform these calculations, it is necessary to use experimental data for at least three tie lines and these should be well separated to cover most of the two phase region. If fewer tie-line data are used, the fitted parameters are somewhat arbitrary although significant improvement in calculated LLE may, nevertheless, be obtained.

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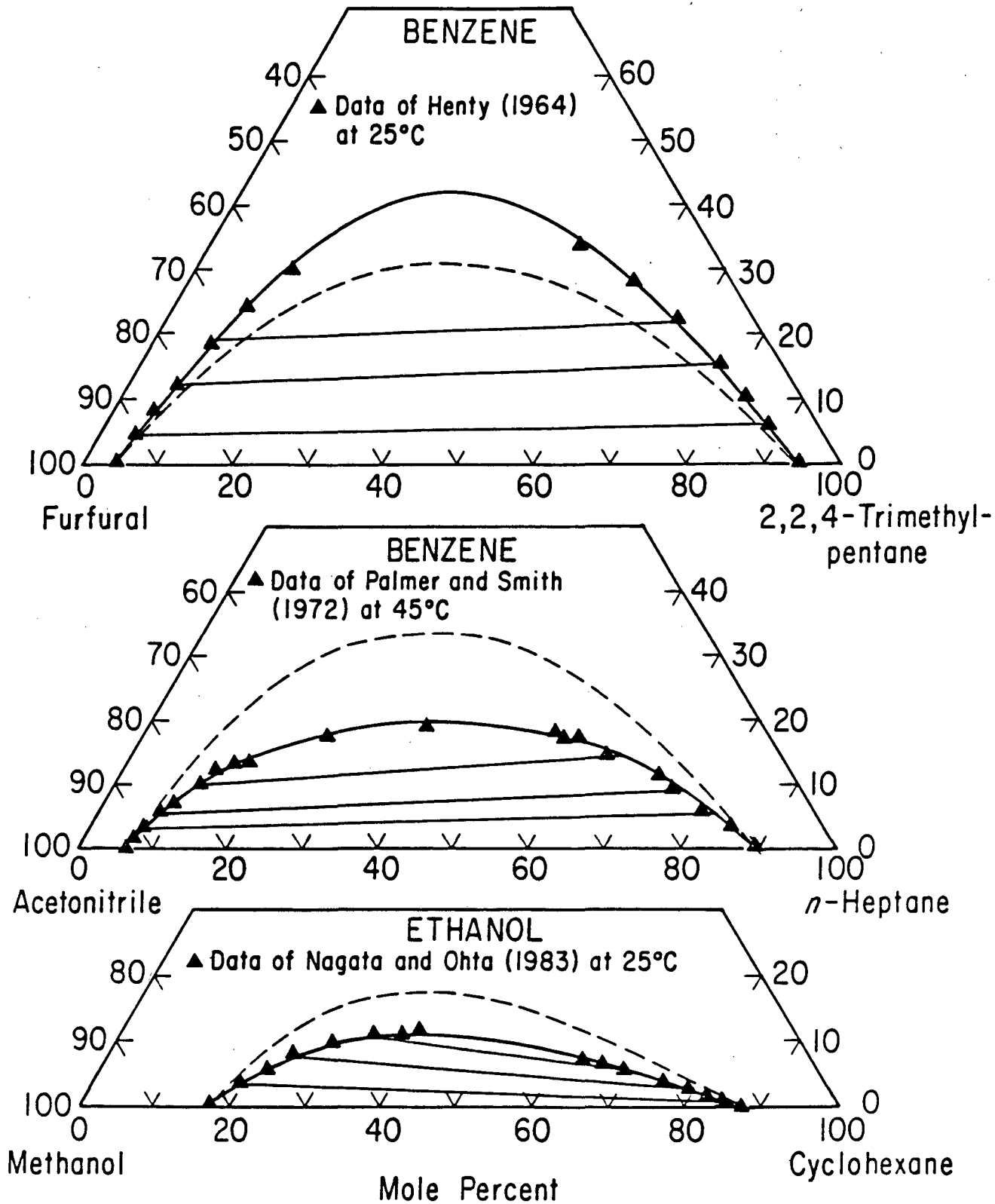
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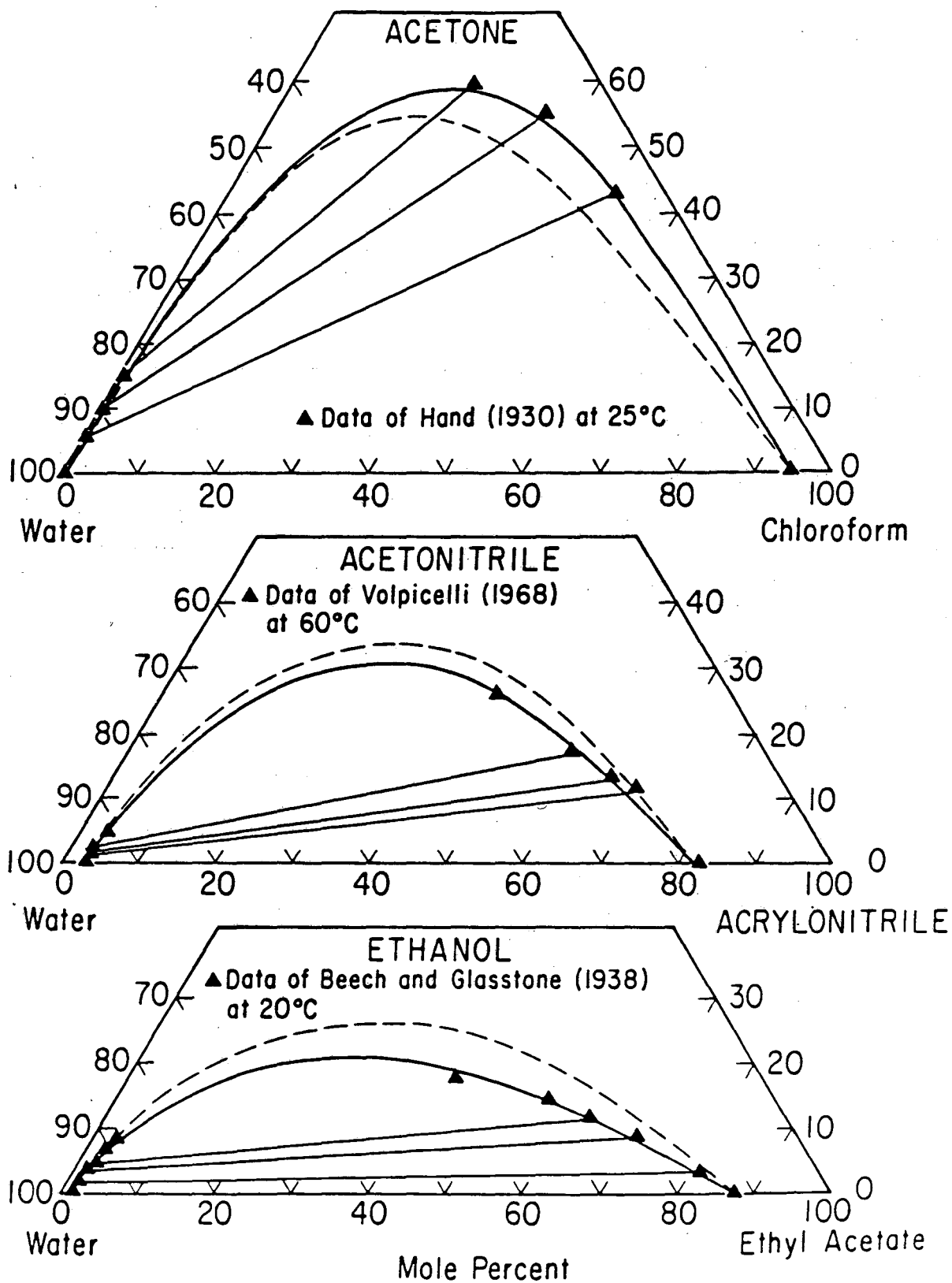
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CALCULATED AND OBSERVED LIQUID-LIQUID EQUILIBRIA

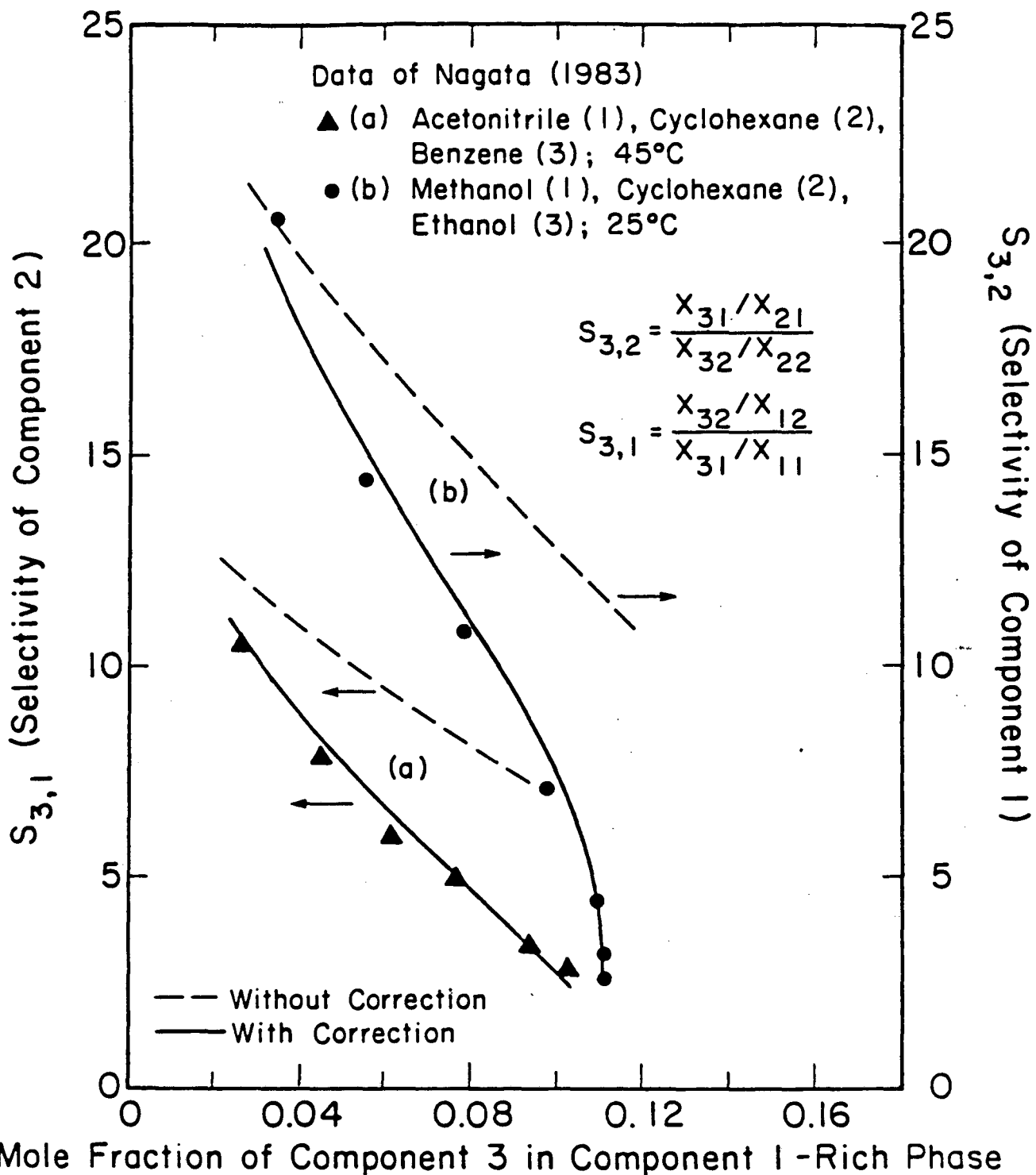
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 — With Correction



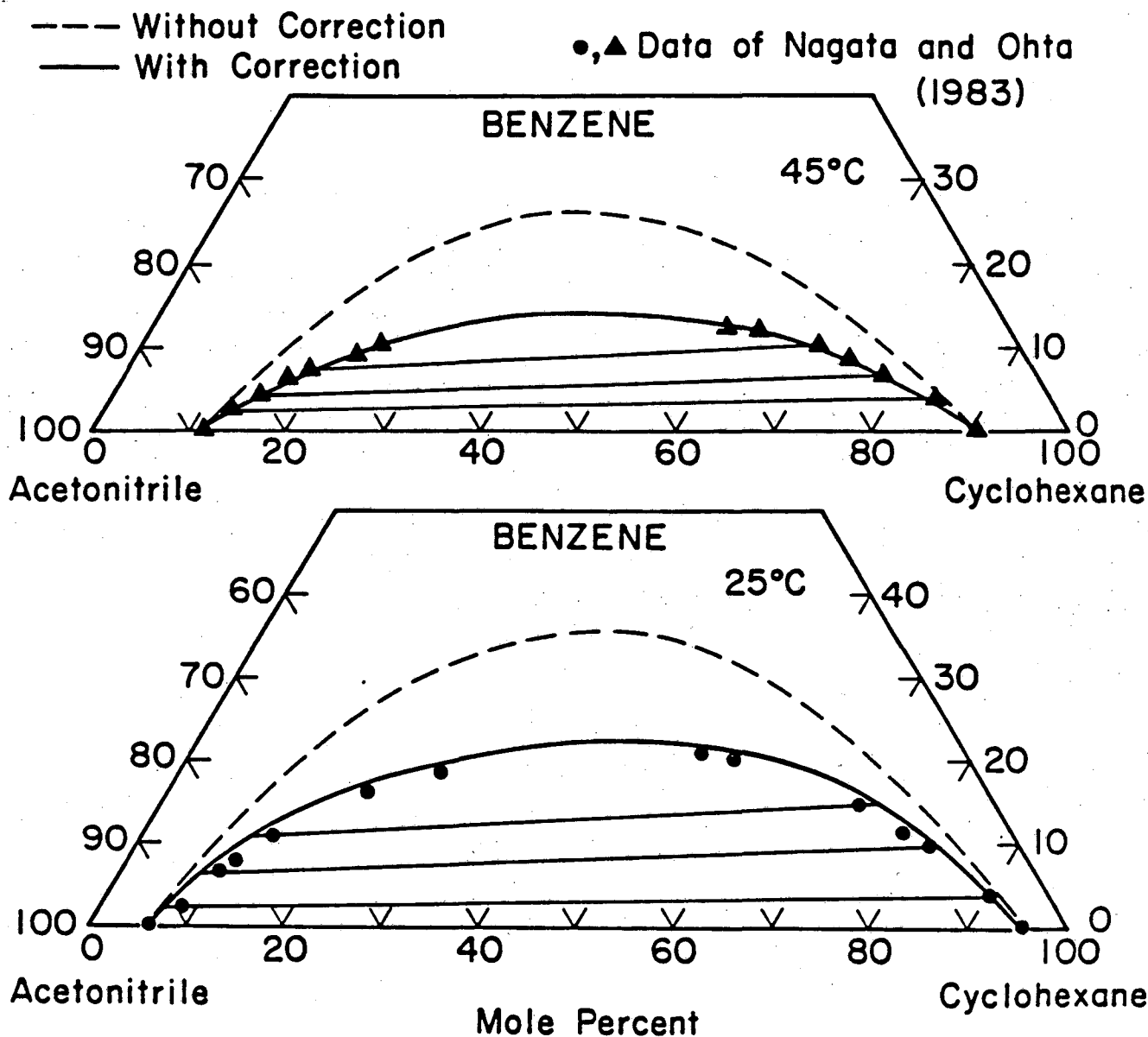
CALCULATED AND OBSERVED LIQUID-LIQUID EQUILIBRIA

Figure 2



CALCULATED SELECTIVITIES IN TWO TERNARY SYSTEMS SHOW LARGE IMPROVEMENTS WHEN TERNARY CORRECTIONS ARE INCORPORATED INTO AN EXCESS GIBBS ENERGY EQUATION

Figure 3



PREDICTED LIQUID-LIQUID EQUILIBRIA FOR ACETONITRILE
(1)-CYCLOHEXANE (2)-BENZENE (3) SYSTEM AT 25°C
USING 1-3 AND 2-3 BINARY PARAMETERS AND TERNARY
CORRECTION PARAMETERS IDENTICAL TO THOSE USED
AT 45°C

Figure 4

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