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TERNARY LIQUID—LIQUID EQUILIBRIA FOR ACETONITRILE—ETHANOL—CYCLOHEXANE AND ACETONITRILE—2-PROPANOL—CYCLOHEXANE

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ABSTRACT

Liquid—liquid equilibrium data were obtained for two ternary systems: acetonitrile—ethanol—cyclohexane at 40°C, and acetonitrile—2-propanol—cyclohexane at 50°C. Binary vapor—liquid equilibrium data were measured for acetonitrile—2-propanol at 50°C. The binary parameters of the Zeta and effective Zeta equations were evaluated from equilibrium data for binary pairs. The parameters obtained were used to predict the ternary liquid—liquid equilibrium data for six systems involving the present systems and the ternary vapor—liquid equilibrium data for one completely miscible system and two partially miscible systems without adding any ternary parameter. A heterogeneous area calculated by the Zeta equation is in general too large and does not decrease appreciably with increasing values of the third parameter ζ of the Zeta equation. However, the effective Zeta equation works much better than the original Zeta equation in data reduction.

NOTATION

a^E	excess molar Helmholtz energy
B	second virial coefficient of a mixture
B_{ij}	second virial coefficient for i—j interaction
g^E	excess molar Gibbs energy
n_T	total number of moles
P	total pressure
P_i^s	vapor pressure of pure component i
R	gas constant
s^E	excess molar entropy
T	absolute temperature
u^E	molar energy of mixing
Δu_{ji}	binary interaction parameter
v	molar volume of a vapor mixture
v_i^L	molar liquid volume of pure component i
x_i	liquid-phase mole fraction of component i

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x_i^I, x_i^{II}	liquid-phase mole fraction of component i in phases I and II
y_i	vapor-phase mole fraction of component i
γ_i	activity coefficient of component i
ζ	proportionality constant
Λ_{ij}	$(v_j^L/v_i^L)\tau_{ji}$
τ_{ji}	$\exp[-\Delta u_{ji}/\zeta RT]$
Φ_i	volume fraction of component i
Φ_{ij}	local volume fraction of molecule i around molecule j
ϕ_i	vapor-phase fugacity coefficient of component i
ϕ_i^s	vapor-phase fugacity coefficient of pure component i at system temperature T and saturation pressure P_i^s

INTRODUCTION

Ternary liquid—liquid equilibrium data provide a severe test for liquid solution models in the calculation of ternary data from binary data. For systems where two binaries are completely miscible and only one binary is partially miscible, reliable calculations are rather difficult. Recently, Nicolaides and Eckert [1] have discussed how well the Zeta equation can correlate equilibrium data of binary mixtures without refering to the question of binary-multicomponent generalization.

In this work, liquid—liquid equilibria were experimentally determined for the two ternary systems ethanol—cyclohexane—acetonitrile at 40°C and 2-propanol—cyclohexane—acetonitrile at 50°C, and for the binary system cyclohexane—acetonitrile at 40 and 50°C. Isothermal vapor—liquid equilibria were measured for 2-propanol—acetonitrile at 50°C. Experimental equilibrium data were compared with calculated values obtained from the Zeta and effective Zeta equations to show the capabilities of these equations in data reduction.

EXPERIMENTAL PROCEDURE

Liquid—liquid equilibria

The upper face of an equilibrium vessel is polished flat and on it a lid is fitted with a Teflon O-ring and is held tightly by six bolts. The lid contains two feed tubes to introduce the second and third components, two sampling tubes, a thermistor and a pressure measuring tube connected to a mercury manometer. Nitrogen gas was used to pressurize the lower sampling tube, so that the mixture could not enter into its during the mixing process.

Binodal curves are determined by the titration method [2] as shown in Fig. 1. First, component 3 is added from a burette to a known amount of component 1 until the mixture becomes turbid. This fixes one point of a mutual solubility data of the binary mixture 1—3, point A. A known amount of component 2 is then added until point B in the miscible region is reached. Component 3 is then added to the mixture until the homogeneous mixture

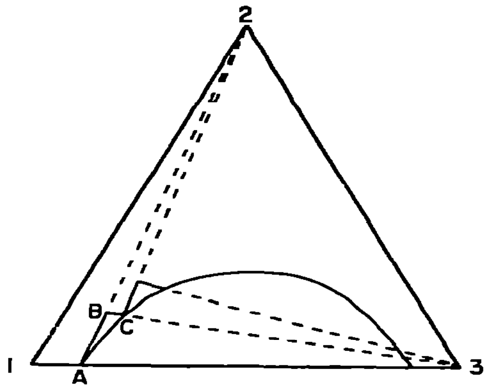

Fig. 1. Binodal curve determination by titration method.

becomes the heterogeneous mixture of point C on the binodal curve. At each step the amount of the added component is always known, so the composition of the mixture is known. During titration, the samples were maintained at a desired temperature within ±0.01°C by means of a water thermostat. Tie line data were determined by the analysis method [2]. A heterogeneous mixture was well mixed with a magnetic stirrer for 2 h to ensure equilibrium between the two liquid phases. After complete separation of the liquid phases, each sample of the coexisting phases was taken by a preheated hypodermic syringe and was analyzed with a Shimadzu model GC-4C gas chromatograph. A 3 m stainless steel column packed with P.E.G. 1000 was used to separate the components of the mixture.

Vapor—liquid equilibria

Vapor—liquid equilibrium data for the 2-propanol—acetonitrile system at 50°C were obtained by using a Scatchard still as described in a previous paper [3]. Vapor and liquid samples were analyzed by the refractive index measurements at 25°C.

Materials

Spectrograde methanol, cyclohexane and reagent grade acetonitrile were used directly. Reagent grade ethanol and 2-propanol were purified by frac-

TABLE 1

Refractive indices of pure component liquids at 25°C

Component	Experimental	Ref. 4
Methanol	1.32658	1.32652
Ethanol	1.35949	1.35941
2-Propanol	1.37512	1.3752
Cyclohexane	1.42352	1.42354
Acetonitrile	1.34170	1.34163

TABLE 2

Comparison of experimental data with literature values of mutual solubility for methanol(1)—cyclohexane(2) at 25°C

x_1^I (cyclohexane-rich phase)	x_1^{II} (methanol-rich phase)	Ref.
0.128	0.825	5
0.1248	0.8280	6
0.1250	0.8281	7
0.1291	0.8284	8
0.1244	0.8285	This work

tional distillation after storage over calcium oxide. The refractive indices of the pure components used for the experimental work are compared with literature values in Table 1.

Results

Table 2 shows a comparison of observed results with literature values of mutual solubility data for the methanol—cyclohexane system at 25°C to check the performance of our apparatus. Tables 3 and 4 represent solubility and tie-line data for the two ternary systems, respectively. Table 5 gives isothermal vapor—liquid equilibrium data for the acetonitrile—2-propanol system at 50°C. The thermodynamic consistency of the data was confirmed by the area test [9].

TABLE 3

Solubility data for ternary systems

x_2	x_3	x_2	x_3	x_2	x_3
Acetonitrile(1)—ethanol(2)—cyclohexane(3) at 40°C					
0.0	0.1039	0.2314	0.2007	0.2008	0.5650
0.0249	0.1132	0.2454	0.2171	0.1712	0.6387
0.0679	0.1205	0.2637	0.2658	0.1377	0.6909
0.1120	0.1343	0.2661	0.3168	0.1020	0.7557
0.1492	0.1479	0.2610	0.3599	0.0686	0.8102
0.1720	0.1570	0.2517	0.4150	0.0	0.9213
0.2124	0.1803	0.2262	0.4942		
Acetonitrile(1)—2-propanol(2)-cyclohexane(3) at 50°C					
0.0	0.1278	0.1126	0.3796	0.0720	0.6686
0.0283	0.1518	0.1118	0.4099	0.0607	0.7129
0.0304	0.1525	0.1088	0.4246	0.0517	0.7438
0.0454	0.1628	0.1056	0.4653	0.0477	0.7578
0.0580	0.1752	0.1014	0.4966	0.0342	0.7996
0.0778	0.1948	0.0936	0.5484	0.0199	0.8396
0.0987	0.2368	0.0874	0.5873	0.0	0.8816
0.1104	0.3190	0.0817	0.6197		

TABLE 4

Tie-line data for ternary systems

Cyclohexane-rich phase		Acetonitrile-rich phase	
x_2^{I}	x_3^{I}	x_2^{II}	x_3^{II}
Acetonitrile(1)—ethanol(2)—cyclohexane(3) at 40°C			
0.0078	0.9080	0.0507	0.1165
0.0195	0.8924	0.1092	0.1339
0.0285	0.8816	0.1502	0.1469
0.0342	0.8717	0.1611	0.1499
0.0377	0.8648	0.1693	0.1535
0.0644	0.8154	0.2183	0.1910
Acetonitrile(1)—2-propanol(2)—cyclohexane(3) at 50°C			
0.0074	0.8686	0.0199	0.1406
0.0189	0.8400	0.0504	0.1728
0.0281	0.8191	0.0702	0.1813
0.0388	0.7910	0.0858	0.2092
0.0561	0.7369	0.1040	0.2576

TABLE 5

Vapor—liquid equilibrium data for the acetonitrile(1)—2-propanol(2) system at 50°C

x_1	y_1	P (mm Hg)	γ_1	γ_2	g^E (cal mole^{-1})
0.047	0.182	210.6	3.274	1.005	38.8
0.127	0.336	242.6	2.555	1.024	89.9
0.164	0.372	253.0	2.278	1.055	115.2
0.220	0.430	265.2	2.051	1.075	137.8
0.236	0.446	268.9	2.008	1.082	144.2
0.301	0.484	277.4	1.759	1.136	166.4
0.431	0.550	288.8	1.448	1.268	189.2
0.546	0.602	294.8	1.275	1.435	190.5
0.637	0.642	296.6	1.171	1.626	178.0
0.763	0.715	293.6	1.078	1.966	139.7
0.864	0.797	285.4	1.032	2.379	93.4
0.900	0.834	281.8	1.025	2.615	75.8
0.932	0.877	273.6	1.012	2.771	51.4
0.948	0.903	269.8	1.011	2.821	41.0
0.987	0.974	257.3	1.001	2.891	9.4

DERIVATION OF EXCESS GIBBS ENERGY

Binary systems

In the derivation of the excess Gibbs energy function, we follow the procedure of Maurer and Prausnitz [10]. We assume that the energy of mixing

u^E of a binary solution of components 1 and 2 is given by

$$u^E = x_1\Phi_{21}\Delta u_{21} + x_2\Phi_{12}\Delta u_{12} \tag{1}$$

and that the local volume fractions are expressed by

$$\Phi_{21} = \Phi_2 \exp(-\Delta u_{21}/\zeta RT)/[\Phi_1 + \Phi_2 \exp(-\Delta u_{21}/\zeta RT)] \tag{2}$$

$$\Phi_{12} = \Phi_1 \exp(-\Delta u_{12}/\zeta RT)/[\Phi_2 + \Phi_1 \exp(-\Delta u_{12}/\zeta RT)] \tag{3}$$

where ζ is a proportionality constant and

$$\Phi_1 = x_1v_1^L/(x_1v_1^L + x_2v_2^L);\text{ and } \Phi_2 = x_2v_2^L/(x_1v_1^L + x_2v_2^L) \tag{4}$$

We may obtain an expression for the molar excess Helmholtz energy a^E from the relation

$$\mathrm{d}(a^E/T)/\mathrm{d}(1/T) = u^E \tag{5}$$

Integrating from $1/T_0$ to $1/T$, we obtain

$$a^E/T = \int_{1/T_0}^{1/T} u^E \mathrm{d}(1/T) + \text{constant} \tag{6}$$

We assume that Δu_{21} and Δu_{12} are independent of temperature. As $1/T_0 \to 0$, we adopt as our boundary condition the Flory—Huggins equation for athermal mixtures of molecules of different size.

$$(a^E/RT)_{\text{athermal}} = -(s^E/R)_{\text{athermal}} = x_1\ln(\Phi_1/x_1) + x_2\ln(\Phi_2/x_2) \tag{7}$$

Then we obtain the excess Gibbs energy g^E under the assumption that at low pressures $(a^E)_{T,V} = (g^E)_{T,P}$.

$$\begin{aligned}(a^E/RT)_{T,V} = (g^E/RT)_{T,P} = -\zeta[x_1 \ln(\Phi_1 + \Phi_2\tau_{21}) + x_2 \ln(\Phi_2 + \Phi_1\tau_{12})] +\\ x_1\ln(\Phi_1/x_1) + x_2 \ln(\Phi_2/x_2)\end{aligned} \tag{8}$$

where

$$\tau_{21} = \exp(-\Delta u_{21}/\zeta RT);\text{ and } \tau_{12} = \exp(-\Delta u_{12}/\zeta RT) \tag{9}$$

Equation (8) is called the effective Zeta equation.

Liquid-phase activity coefficients are obtained by

$$RT \ln \gamma_i = (\partial n_T g^E/\partial n_i)_{T,P,n_j(j\neq i)} \tag{10}$$

where n_i is the number of moles of component i, n_T is the total number of moles

$$x_i = n_i/n_T = n_i/\sum_{i=1}^{n} n_i$$

Thus

$$\begin{aligned}\ln \gamma_1 = \zeta\left[-\ln(x_1 + \Lambda_{12}x_2) + x_2\left\{\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right\}\right]\\ + \left[\ln\left(\frac{\Phi_1}{x_1}\right) + 1 - \frac{\Phi_1}{x_1}\right](1-\zeta)\end{aligned} \tag{11}$$

$$\ln \gamma_2 = \zeta\left[-\ln(x_2 + \Lambda_{21}x_1) - x_1\left\{\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right\}\right] + \left[\ln\left(\frac{\Phi_2}{x_2}\right) + 1 - \frac{\Phi_2}{x_2}\right](1 - \zeta) \tag{12}$$

where

$$\Lambda_{12} = (v_2^L/v_1^L)\tau_{21}; \text{ and } \Lambda_{21} = (v_1^L/v_2^L)\tau_{12} \tag{13}$$

If $\zeta = 1$, eqns. (11) and (12) reduce to the Wilson equation [11]. Replacing eqn. (1) by

$$u^E = x_1 v_1^L \Phi_{21} \Delta u_{21} + x_2 v_2^L \Phi_{12} \Delta u_{12} \tag{14}$$

and following the derivation method described above, we can easily derive the Zeta equation described by Nicolaides and Eckert [1]

$$g^E/RT = -\zeta[x_1 v_1^L \ln(\Phi_1 + \Phi_2\tau_{21}) + x_2 v_2^L \ln(\Phi_2 + \Phi_1\tau_{12})] + x_1 \ln(\Phi_1/x_1) + x_2 \ln(\Phi_2/x_2) \tag{15}$$

$$\ln \gamma_1 = \zeta\left[-v_1^L \ln(\Phi_1 + \Phi_2\tau_{21}) + v_1^L\Phi_2\left\{\frac{\tau_{21}}{\Phi_1 + \Phi_2\tau_{21}} - \frac{\tau_{12}}{\Phi_2 + \Phi_1\tau_{12}}\right\}\right] + \ln\left(\frac{\Phi_1}{x_1}\right) + 1 - \frac{\Phi_1}{x_1} \tag{16}$$

$$\ln \gamma_2 = \zeta\left[-v_2^L \ln(\Phi_2 + \Phi_1\tau_{12}) + v_2^L\Phi_1\left\{\frac{\tau_{12}}{\Phi_2 + \Phi_1\tau_{12}} - \frac{\tau_{21}}{\Phi_1 + \Phi_2\tau_{21}}\right\}\right] + \ln\left(\frac{\Phi_2}{x_2}\right) + 1 - \frac{\Phi_2}{x_2} \tag{17}$$

Multicomponent systems

Apparently, eqns. (8) and (15) can be extended to multicomponent mixtures with an additional assumption that ζ is the same for all those binaries which comprise a multicomponent mixture.

The effective Zeta equation for g^E is expressed by

$$g^E/RT = -\zeta \sum_{i=1}^{n} x_i \ln\left(\sum_{j=1}^{n} x_j\tau_{ji}\right) + \sum_{i=1}^{n} x_i \ln(\Phi_i/x_i) \tag{18}$$

and the activity coefficient of component i is

$$\ln \gamma_i = \zeta\left\{-\ln\left(\sum_{j=1}^{n} x_j\Lambda_{ij}\right) + 1 - \sum_{k=1}^{n}\left[\frac{x_k\Lambda_{ki}}{\sum_{j=1}^{n} x_j\Lambda_{kj}}\right]\right\} + \left[\ln\left(\frac{\Phi_i}{x_i}\right) + 1 - \frac{\Phi_i}{x_i}\right] \times (1 - \zeta) \tag{19}$$

In eqns. (18) and (19) τ_{ji} and Λ_{ij} are given by

$$\tau_{ji} = \exp[-\Delta u_{ji}/\zeta RT] \tag{20}$$

$$\Lambda_{ij} = (v_j^L/v_i^L)\tau_{ji} \tag{21}$$

Similarly, the Zeta equation has the following forms for g^E and γ_i

$$g^E/RT = -\zeta \sum_{i=1}^{n} x_i v_i^L \ln\left(\sum_{j=1}^{n} \Phi_j \tau_{ji}\right) + \sum_{i=1}^{n} x_i \ln(\Phi_i/x_i) \tag{22}$$

$$\ln \gamma_i = \zeta \left\{ -v_i^L \ln\left(\sum_{j=1}^{n} \Phi_j \tau_{ji}\right) + v_i^L - v_i^L \sum_{j=1}^{n} \left[\frac{\Phi_j \tau_{ij}}{\sum_{k=1}^{n} \Phi_k \tau_{kj}}\right]\right\}$$

$$+ \ln\left(\frac{\Phi_i}{x_i}\right) + 1 - \frac{\Phi_i}{x_i} \tag{23}$$

DETERMINATION OF BINARY PARAMETERS

A total of seven parameters is required for the prediction of the ternary phase equilibria, because the ζ parameter should be the same value for the three component binary systems comprising a ternary system under consideration. These binary parameters could be obtained from the existing thermodynamic properties: vapor—liquid equilibrium data, solubility data, heats of mixing, and activity coefficients at infinite dilution. In the ternary systems studied in this work only one binary system shows immiscibility, so one set of parameters can be derived from solubility data. The two other binary parameter sets are derived from vapor—liquid equilibrium data.

First, the ζ parameter should have a preset value. For a partially miscible system, only two energy parameters can be determined by solving the equation

$$x_1^I \gamma_1^I = x_1^{II} \gamma_1^{II}; \text{ and } x_2^I \gamma_2^I = x_2^{II} \gamma_2^{II} \tag{24}$$

where the superscripts represent two liquid phases, I and II. For two completely miscible systems, two sets of parameters are obtained by minimizing the sum of squares of deviations in $\ln(\gamma_1/\gamma_2)$ for all available data points. For this purpose the Simplex method of Nelder and Mead [12] was used.

The basic vapor—liquid equilibrium relationship for nonideal vapor and liquid phases is given by

$$\phi_i y_i P = \gamma_i x_i \phi_i^s P_i^s \exp[(P - P_i^s) v_i^L / RT] \tag{25}$$

where y_i is the vapor-phase mole fraction of component i, ϕ_i is the vapor-phase fugacity coefficient, P is the total pressure and P_i^s is the saturation pressure. At normal pressures the vapor-phase fugacity coefficient is expressed by

$$\ln \phi_i = (P/RT)\,(2 \sum_{j=1}^{n} y_i B_{ij} - B) \tag{26}$$

Equation (26) is derived by use of the volume explicit virial equation truncated after the second term [9].

$$Pv/RT = 1 + BP/RT \tag{27}$$

where v is the molar volume of the vapor mixture and B is the second virial coefficient of the mixture of n components. B is calculated from the pure-component and cross-virial coefficients B_{ij}.

$$B = \sum_{i=1}^{n} \sum_{j=1}^{n} y_i y_j B_{ij} \tag{28}$$

For pure component i, eqn. (26) reduces to the fugacity coefficient of pure vapor i at temperature T and saturation pressure P_i^s

$$\ln \phi_i^s = B_{ii} P_i^s / RT \tag{29}$$

The generalized correlation of Hayden and O'Connell [13] may be used to calculate the virial coefficients.

CALCULATED RESULTS

Figure 2 shows curves comparing calculated vapor composition as determined from complete isothermal x—y—P data for the original Zeta and effective Zeta equations. The effective Zeta equation is evidently superior to the original Zeta equation, which erroneously predicts phase separation for the ethanol—cyclohexane system at 35°C regardless of the various values of ζ. Table 6 lists a number of parameters for representative binary systems. Figure 3 illustrates the data of the acetonitrile—2-propanol system represented by the effective Zeta equation. When the effective Zeta equation is

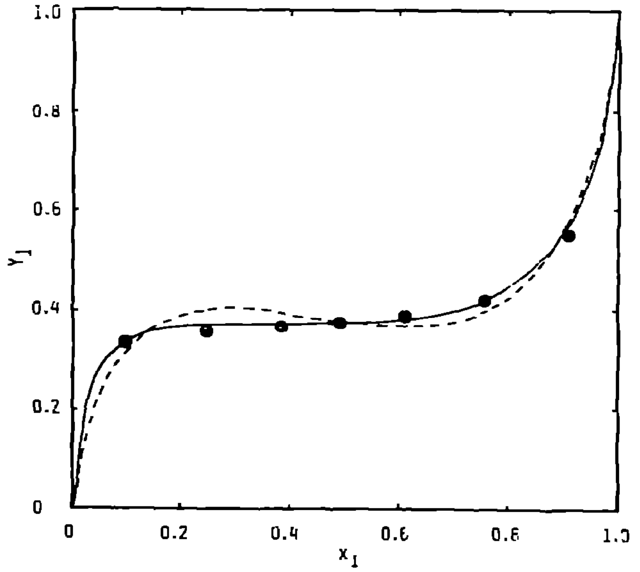

Fig. 2. Calculated vapor composition from x—y—P data for the ethanol(1)—cyclohexane(2) system at 35°C: ●, data of ref. 14; ———, effective Zeta eqn. (ζ = 7.0), - - - - - -, Zeta eqn. (ζ = 0 9).

TABLE 6

Binary parameters and results of correlation of vapor—liquid equilibria by Zeta and effective Zeta equations

System (1—2)	Temp (°C)	No. of data points	Eqn. *	Parameters			Root mean square deviation			Ref.
				$g_{21}-g_{11}$ (cal mole^{-1})	$g_{12}-g_{22}$ (cal mole^{-1})	ζ	Relative pressure (×1000)	Vapor mole fraction (×1000)	Pressure (mm Hg)	
Ethyl acetate—ethanol	40.0	14	1	−138.52	168.79	0.9	8.9	3.6	1.8	15
			1	−258.77	299.22	2.0	8.6	4.0	1.7	
			2	−646.06	1189.19	2.4	9.8	2.4	1.9	
Ethanol—water	25.0	19	1	−190.26	275.39	0.9	5.8	4.1	0.3	16
			1	−378.91	493.04	2.0	4.6	3.3	0.2	
			2	−1968.51	2188.52	2.4	17.7	12.9	0.7	
			2	−1287.93	1291.89	3.6	44.8	30.2	1.9	
	40.0	13	1	−187.15	271.06	0.9	31.3	6.0	2.4	15
			1	−375.55	486.93	2.0	30.7	6.3	2.4	
			2	−1945.62	2142.34	2.4	38.3	6.4	3.0	
Acetonitrile—benzene	45.0	11	1	188.12	−152.16	0.9	12.1	12.5	3.3	17
			1	332.35	−284.26	2.0	12.6	13.0	3.4	
			2	1422.25	−817.02	2.4	9.4	10.0	2.5	
			2	2960.51	−2329.98	4.4	7.4	8.3	2.0	
Benzene—*n*-heptane	45.0	15	1	−58.07	64.98	0.9	9.3	3.2	1.8	17
			1	−105.32	113.64	2.0	9.3	3.1	1.8	
			2	44.34	511.82	2.4	9.3	3.2	1.8	
			2	−61.96	686.86	4.4	9.3	3.2	1.8	
Chloroform—acetone	25.0	7	1	−86.20	86.56	0.9	31.9	11.6	5.3	18
			1	−119.96	119.46	2.0	34.9	12.5	5.8	
			2	−658.77	166.36	2.4	21.3	10.8	3.5	
			2	−673.93	179.92	2.5	20.9	10.7	3.5	
Acetone—water	25.0	13	1	−238.57	367.91	0.9	40.6	8.0	6.6	19
			1	−461.67	629.70	2.0	46.8	8.4	7.6	
			2	−3268.04	5828.36	2.4	132.6	43.8	13.1	
			2	−3478.13	6181.38	2.5	150.7	48.1	14.6	

Ethanol—benzene	20.0	13	1	234.66	−180.11	0.9	55.6	21.9	5.0	20
			1	410.45	−337.04	2.0	55.0	22.6	4.9	
			2	1699.21	−623.47	2.4	59.4	20.1	5.4	
			2	2305.62	−1251.98	3.6	58.9	20.1	5.4	
	45.0	12	1	265.77	−202.12	0.9	24.6	19.7	7.2	21
			1	461.24	−375.41	2.0	26.4	21.1	7.7	
			2	2187.70	−786.94	2.4	12.0	10.5	3.5	
			2	2954.09	−1544.50	3.6	11.9	10.6	3.5	
Methanol—tetrachloromethane	55.0	6	1	429.78	−294.15	0.9	85.1	57.2	59.2	22
			1	737.74	−554.05	2.0	91.9	60.5	64.0	
			2	3703.20	−1868.73	2.4	28.9	22.6	19.2	
Tetrachloromethane—benzene	40.0	8	1	−58.11	62.13	0.9	7.4	1.0	1.5	23
			1	−54.31	56.18	2.0	7.2	1.6	1.5	
			2	−331.59	425.18	2.4	7.3	1.0	1.5	
	70.0	8	1	−54.74	58.08	0.9	4.9	0.7	3.0	23
			1	−54.31	56.18	2.0	5.1	1.1	3.1	
			2	−313.91	398.21	2.4	4.9	0.7	3.0	
Methanol—benzene	55.0	9	1	361.54	−256.99	0.9	37.2	31.1	21.7	24
			1	625.52	−484.56	2.0	41.1	34.1	24.1	
			2	2903.78	−1505.11	2.4	16.7	11.9	10.1	
Acetonitrile—2-propanol	50.0	15	1	171.72	−138.84	0.9	14.2	4.6	3.7	This work
			1	306.92	−263.29	2.0	14.1	4.9	3.6	
			2	1121.96	−375.02	2.4	13.7	3.5	3.6	
			2	3971.16	−3296.08	8.5	13.6	2.8	3.6	
Cyclohexane—2-propanol	50.0	9	1	−189.44	242.38	0.9	27.4	22.0	9.0	25
			1	−349.61	419.79	2.0	28.6	23.0	9.5	
			2	−594.04	2056.79	2.4	19.4	15.1	6.3	
			2	−3974.78	5669.32	8.5	19.0	14.7	6.2	
Acetonitrile—ethanol	40.0	14	1	106.77	−84.76	0.9	9.8	5.6	1.9	26
			1	201.70	−173.74	2.0	9.7	5.6	1.9	
			2	739.56	101.82	2.4	9.9	5.2	1.9	
			2	1319.54	−514.84	7.0	9.9	5.5	1.9	
Ethanol—cyclohexane	35.0	7	1	270.02	−202.29	0.9	34.7	28.4	7.0	14
			1	467.34	−377.53	2.0	37.5	30.1	7.6	
			2	2308.17	−823.91	2.4	22.0	17.2	4.3	
			2	6763.93	−4897.05	7.0	16.3	10.0	3.4	

TABLE 6 (continued)

System (1—2)	Temp (°C)	No. of data points	Eqn. *	Parameters			Root mean square deviation			Ref.
				$g_{21}-g_{11}$ (cal mole^{-1})	$g_{12}-g_{22}$ (cal mole^{-1})	ζ	Relative pressure (×1000)	Vapor mole fraction (×1000)	Pressure (mm Hg)	
	50.0	7	1	276.67	−208.40	0.9	32.9	27.7	12.7	14
			1	479.59	−389.91	2.0	34.9	29.5	13.6	
			2	2357.53	−855.05	2.4	18.5	16.3	6.9	
			2	7031.18	−5135.59	7.0	9.2	8.6	3.4	
Ethyl acetate—water	40.0	S **	1	−250.48	417.33	0.9				15
			1	−507.23	727.01	2.0				
			2	−3199.26	4331.20	2.4				
Acetonitrile—*n*-heptane	45.0	S	1	302.17	−219.09	0.9				17
			1	529.77	−417.76	2.0				
			2	2407.67	−856.45	2.4				
			2	5427.59	−4055.94	4.4				
Chloroform—water	25.0	S	1	−272.00	527.17	0.9				27
			1	−568.90	902.40	2.0				
			2	−639.20	3330.69	2.4				
			2	−849.21	3405.75	2.5				
Benzene—water	25.0	S	1	−294.56	604.55	0.9				4
			1	−617.80	1022.17	2.0				
			2	−588.78	3993.73	2.4				
			2	−3928.60	6148.68	3.6				
Acetonitrile—cyclohexane	40.0	S	1	295.59	−213.59	0.9				This work
			1	520.53	−409.68	2.0				
			2	2264.77	−462.48	2.4				
			2	6565.20	−4959.52	7.0				
	50.0	S	1	283.06	−208.08	0.9				This work
			1	500.54	−399.16	2.0				
			2	2129.25	−454.29	2.4				
			2	8935.79	−6964.25	8.5				

* Eqn. (1) = Zeta eqn.; eqn. (2) = effective Zeta eqn.

** S = solubility data.

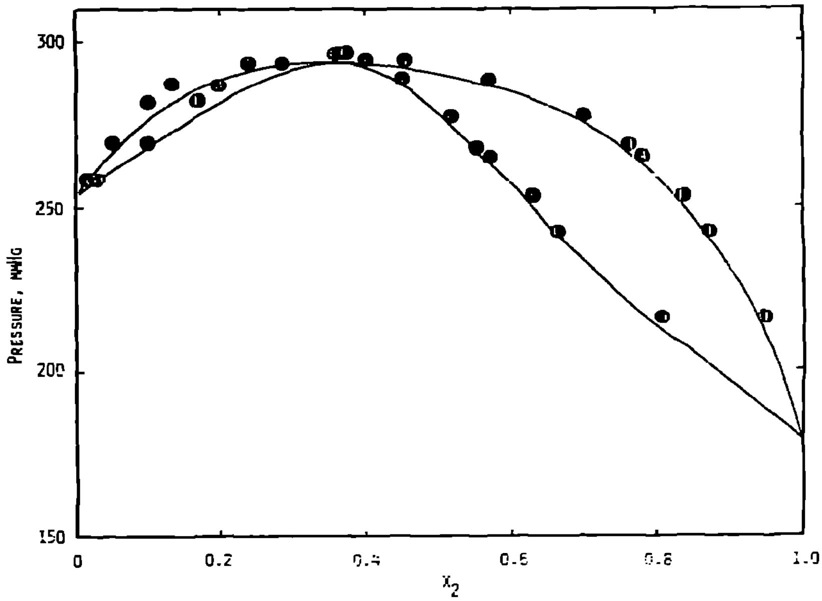

Fig. 3. Vapor—liquid equilibria for the acetonitrile(1)—2-propanol(2) system at 50°C: ●, data of this work; ———, effective Zeta eqn. (ζ = 2.4—8.5).

used in the correlation of ternary liquid—liquid equilibrium data, increasing the value of ζ decreases the total surface of the predicted heterogeneous area. Increasing it to the highest possible value, it is possible to bring the cal-

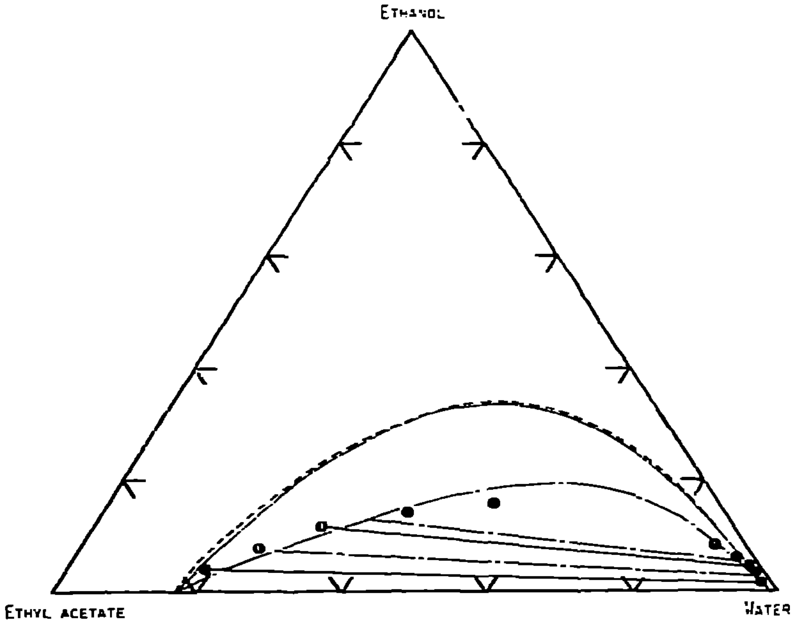

Fig. 4. Ternary liquid—liquid equilibria for the ethyl acetate(1)—ethanol(2)—water(3) system at 40°C: ●, data of ref. 15; ———, Zeta eqn. (ζ = 0.9); - - - - - -, Zeta eqn. (ζ = 2.0); - — - — -, effective Zeta eqn. (ζ = 2.4).

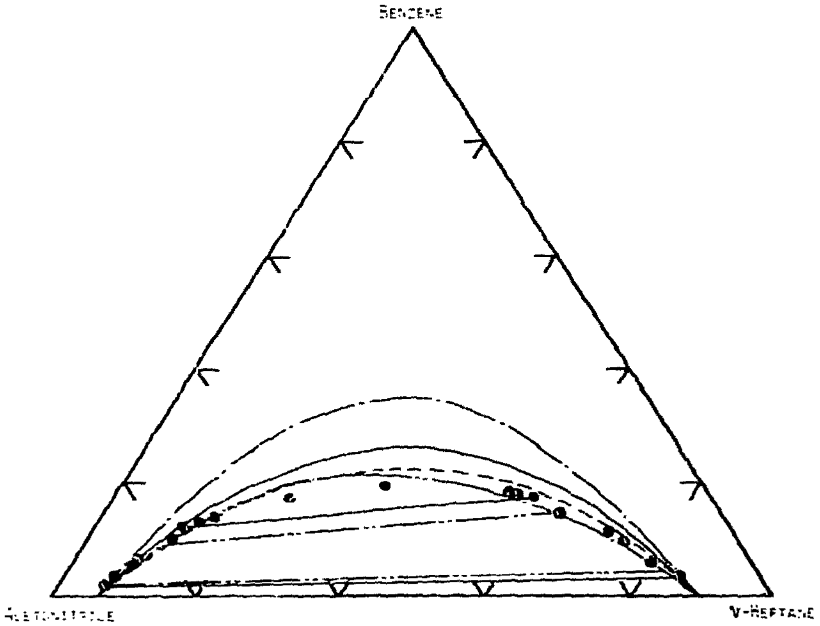

Fig. 5. Ternary liquid–liquid equilibria for the acetonitrile(1)–benzene(2)–*n*-heptane(3) system at 45°C: ●, data of ref. 17; ———, Zeta eqn. ($\zeta = 0.9$); - - - - - - Zeta eqn. ($\zeta = 2.0$); - — - — -, effective Zeta eqn. ($\zeta = 2.4$); — - - — - - —, effective Zeta eqn. ($\zeta = 4.4$).

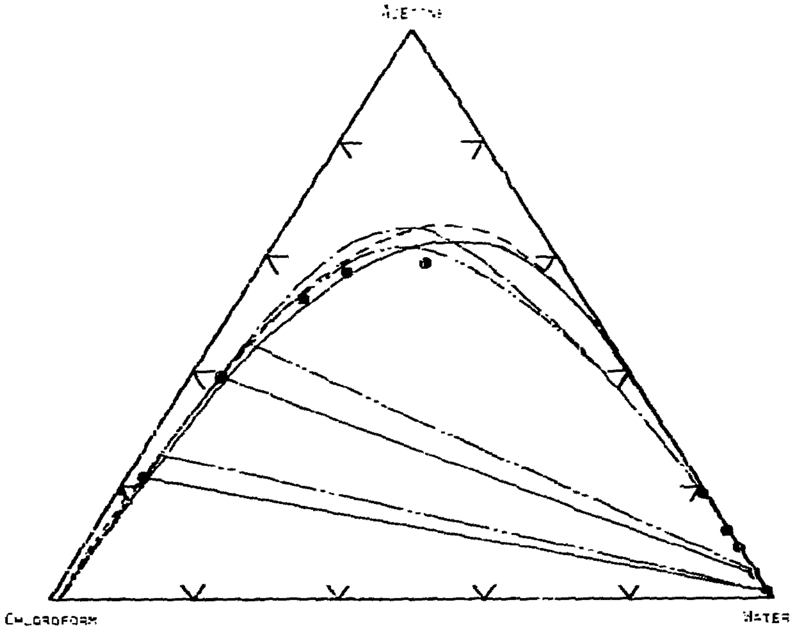

Fig. 6. Ternary liquid–liquid equilibria for the chloroform(1)–acetone(2)–water(3) system at 25°C: ●, data of ref. 27; ———, Zeta eqn. ($\zeta = 0.9$); - - - - - -, Zeta eqn. ($\zeta = 2.0$); - — - — -, effective Zeta eqn. ($\zeta = 2.4$); — - - — - - —, effective Zeta eqn. ($\zeta = 2.5$).

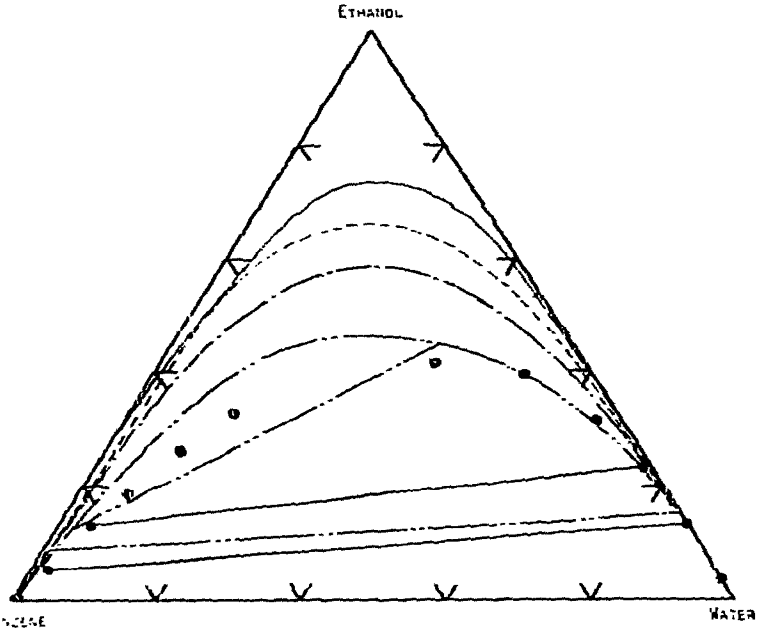

Fig. 7. Ternary liquid–liquid equilibria for the benzene(1)–ethanol(2)–water(3) system at 25°C: ●, data of ref. 28; ———, Zeta eqn. ($\zeta = 0.9$); - - - - - -, Zeta eqn. ($\zeta = 2.0$); - — - — -, effective Zeta eqn. ($\zeta = 2.4$); — - - — - - —, effective Zeta eqn. ($\zeta = 3.6$).

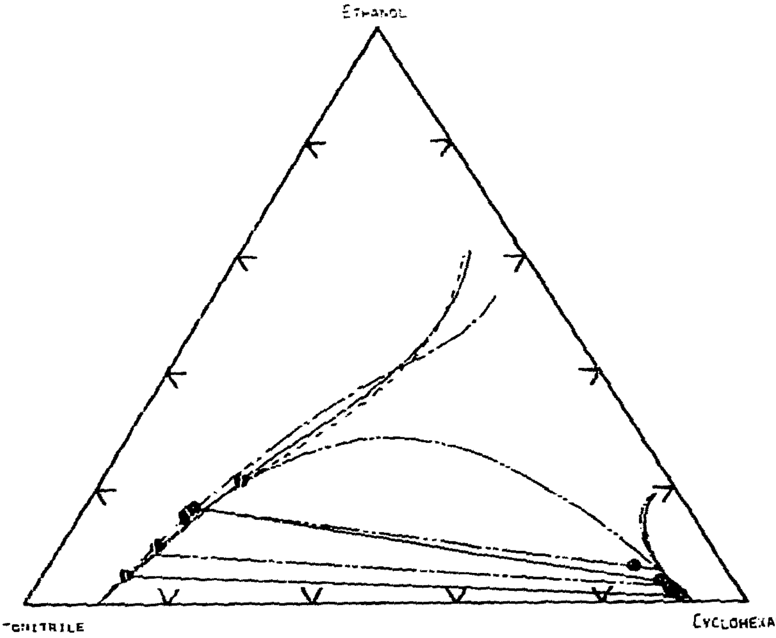

Fig. 8. Ternary liquid–liquid equilibria for the acetonitrile(1)–ethanol(2)–cyclohexane(3) system at 40°C: ●, data of this work; ———, Zeta eqn. ($\zeta = 0.9$); - - - - - -, Zeta eqn. ($\zeta = 2.0$); - — - — -, effective Zeta eqn. ($\zeta = 2.4$); — - - — - - —, effective Zeta eqn. ($\zeta = 7.0$).

TABLE 7

Predicted results for ternary vapor—liquid equilibria

System	Temp. (°C)	No. of data points	Eqn. *	ζ	Absolute arithmetic deviation				Ref.
					Vapor mole fraction (×1000)			Pressure (mm Hg)	
					Δy_1	Δy_2	Δy_3		
Ethyl acetate(1)—ethanol(2)—water(3)	40.0	9	1	0.9	39.9	22.2	28.8	12.9	15
			1	2.0	40.9	23.0	29.3	13.3	
			2	2.4	17.2	11.0	13.8	5.2	
Methanol(1)—tetrachloromethane(2)—benzene(3)	55.0	8	1	0.9	52.3	23.7	28.9	50.3	22
			1	2.0	59.2	27.1	32.1	56.9	
			2	2.4	11.5	5.5	6.6	11.9	
Acetonitrile(1)—benzene(2)—*n*-heptane(3)	45.0	51	1	0.9	22.6	21.3	19.3	13.3	17
			1	2.0	29.6	29.8	25.7	21.5	
			2	2.4	12.7	4.8	10.3	6.0	
			2	4.4	14.6	12.4	11.2	10.6	

* Eqn. (1) = Zeta eqn.; eqn. (2) = effective Zeta eqn.

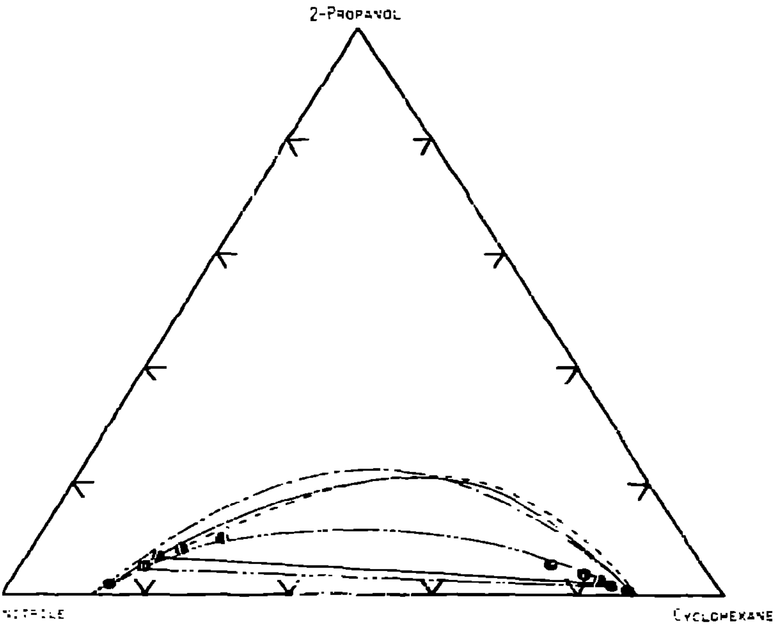

Fig. 9. Ternary liquid—liquid equilibria for the acetonitrile(1)—2-propanol(2)—cyclohexane(3) system at 50°C: ●, data of this work; ———, Zeta eqn. ($\zeta = 0.9$); - - - - - -, Zeta eqn. ($\zeta = 2.0$); —·—·—, effective Zeta eqn. ($\zeta = 2.4$); —··—··—, effective Zeta eqn. ($\zeta = 8.5$).

culated binodal close to the experimental one. The value of ζ is not a universal constant and depends on each chosen ternary system. ζ varied within a range of 2.4—8.5 for the six systems studied in this work. However, this is not the case for the Zeta equation. We notice that increasing the ζ value has little influence on the position of the binodal. Figures 4—9 show agreement between experimental data and calculated results obtained with the two equations. The binary interaction parameters of the three systems (ethanol—benzene at 25°C, ethanol—cyclohexane at 40°C, and tetrachloromethane—benzene at 55°C) were estimated by linear interpolation. Table 7 shows the results of prediction of the vapor—liquid equilibrium in the ternary systems from binary data. Again the superiority of the effective Zeta equation is evident. In conclusion, the effective Zeta equation is more suitable than the original Zeta equation for reproducing binary and ternary phase equilibrium data for the systems studied in this work.

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REFERENCES

1 G.L. Nicolaides and C.A. Eckert, Ind. Eng. Chem., Fundam., 17 (1978) 331.
2 L. Alders, Liquid—Liquid Extraction, 2nd edn., Elsevier, Amsterdam, 1959.
3 I. Nagata, T. Ohta, M. Ogura and S. Yasuda, J. Chem. Eng. Data, 21 (1976) 310.
4 J.A. Riddick and W.B. Bunger, Organic Solvents, 3rd edn., Wiley-Interscience, New York, 1970.
5 D.C. Jones and S. Amstell, J. Chem. Soc., (1930) 1316.
6 R.W. Kister, G.D. Jonson and M.D. Shelter, J. Chem. Eng. Data, 6 (1961) 338.
7 M. Yasuda, H. Kawade and T. Katayama, Kagaku Kogaku Ronbunshu, 1 (1975) 172.
8 S.T. Takeuchi, T. Nitta and T. Katayama, J. Chem. Eng. Jpn., 8 (1975) 248.
9 J.M. Prausnitz, Molecular Thermodynamics of Fluid-Phase Equilibria, Prentice Hall, Englewood Cliffs, N.J., 1969.
10 G. Maurer and J.M. Prausnitz, Fluid Phase Equilibria, 2 (1978) 91.
11 G.M. Wilson, J. Am. Chem. Soc., 86 (1964) 127.
12 J.A. Nelder and R. Mead, Computer J., 7 (1965) 308.
13 J.G. Hayden and J.P. O'Connell, Ind. Eng. Chem. Process Des. Dev., 14 (1975) 209.
14 G. Scatchard and F.G. Satkiewicz, J. Am. Chem. Soc., 86 (1964) 130.
15 I. Mertl, Collect. Czech. Chem. Commun., 37 (1972) 366.
16 J.A. Larkin and R.C. Pemberton, Nat. Phys. Lab. Rep. Chem. 43, January, 1976.
17 D.A. Palmer and B.D. Smith, J. Chem. Eng. Data, 17 (1972) 71.
18 C.R. Mueller and E.R. Kearns, J. Phys. Chem., 62 (1958) 1441.
19 W.G. Beare, G.A. McVicar and J.B. Ferguson, J. Phys. Chem., 34 (1930) 1310.
20 J.J. Kipling and D.A. Tester, J. Chem. Soc., (1952) 4123.
21 I. Brown and F. Smith, Aust. J. Chem., 7 (1954) 264.
22 G. Scatchard and L.B. Ticknor, J. Am. Chem. Soc., 74 (1952) 3724.
23 G. Scatchard, S.E. Wood and J.M. Mochel, J. Am. Chem. Soc., 62 (1940) 712.
24 G. Scatchard, S.E. Wood and J.M. Mochel, J. Am. Chem. Soc., 68 (1946) 1957.
25 I. Nagata, T. Ohta and Y. Uchiyama, J. Chem. Eng. Data, 18 (1973) 54.
26 H. Sugi and T. Katayama, J. Chem. Eng. Jpn., 11 (1978) 167.
27 W. Reinders and C.H. De Minjer, Rec. Trav. Chim., 66 (1947) 573.
28 W.D. Bancroft and S.S. Hubard, J. Am. Chem. Soc., 64 (1942) 347.