found to be linear from 0 to 10 wt % styrene monomer in toluene.

The sound velocity-concentration relationships of the polymer and monomer in toluene, presented in Figure 2, are very different. The monomer curve has a smaller initial slope than the polymer curve and is linear. The polymer curve, however, exhibits slight upward curvature. The polymer curve represents polystyrenes having molecular weights between 9100 and 1 840 000. Between the monomer curve and polymer curve, a series of curves should exist which corresponds to molecular weights between 104, the molecular weight of the monomer, and 9100. The determination of these intermediate curves was beyond the scope of this study.

Conclusions

On the basis of the experimental measurements of this study, the following conclusions can be drawn:

(1) Sound velocity and density of 0–10 wt % solutions of polystyrene in toluene are independent of polymer molecular weight over the range from 9100 to 1 840 000.

(2) The sound velocity–concentration relationship for polystyrene in toluene from 0 to 20 wt % can be accurately described by using a second-order polynomial.

(3) The density–concentration relationship for polystyrene in toluene from 0 to 13 wt % is linear within experimental error.

(4) Toluene solutions of styrene monomer and polystyrenes having molecular weights greater than 9100 have measurably different sound velocity–concentration relationships. The polymer curve is concave and has a greater initial slope than the monomer curve which is a linear function of concentration.

Acknowledgment

We gratefully acknowledge T. C. Klingler and A. Platt of Dow Chemical for determining the number average and weight average molecular weight values for the polystyrene B sample.

Registry No. Polystyrene (homopolymer), 9003-53-6; styrene, 100-42-5.

Literature Cited

(1) Nozdrev, V. F. "Application of Ultrasonics in Molecular Physics"; Gordan and Breach: New York, 1963.
(2) Synder, S. J.; Synder, J. R. *J. Chem. Eng. Data* **1974**, *19*, 270.
(3) Bader, M.; Cerf, R. *Acustica* **1970**, *23*, 31.
(4) Dunbar, J. I.; North, A. M.; Pethrick, R. A.; Steinhauer, D. B. *J. Polymn. Sci., Polymn. Phys. Ed.* **1977**, *15*, 263.
(5) Cochran, M. A.; Dunbar, J. H.; North, A. M.; Pethrick, R. A. *J. Chem. Soc., Faraday Trans 2* **1974**, *70*, 215.
(6) Lipkin, M. R.; Davison, J. A.; Harvey, W. T.; Kurtz, S. S. *Ind. Eng. Chem.* **1944**, *16*, 55.
(7) Freyer, E. B.; Hubbard, J. C.; Andrews, D. H. *J. Am. Chem. Soc.* **1929**, *51*, 759.

Received for review May 16, 1983. Accepted August 29, 1983.

Vapor–Liquid Equilibria of the Ternary System Methyl Borate–Methyl Alcohol–Benzene

Nicolai Münster, Charles A. Plank,* Walden L. S. Laukhuf, and Phoebus M. Christopher
Department of Chemical and Environmental Engineering, University of Louisville, Louisville, Kentucky 40292

Vapor–liquid equilibrium measurements at 101 325 Pa are reported for the methyl borate–methyl alcohol–benzene system. Analysis of the results shows that the ternary system can be reasonably represented from binary data by the Wilson equations and slightly better by the Margules correlations. The ternary system is made up of two minimum-boiling azeotropic systems and one ideal binary system. No ternary azeotrope exists.

The vapor–liquid equilbria have been measured for the ternary system methyl borate–methyl alcohol–benzene at 101 325 ± 133 Pa (760 ± 1 torr). An Altsheler (circulation type) still was used and is described in detail by Hala et al. (*1*). The present version, however, contains two thermocouples, one near the surface of the boiling liquid and one in the vapor space directly above the liquid level. These two thermocouples were both calibrated and in general gave the same values during operation. When they differed, the liquid thermocouple temperature was reported. Temperatures are believed to be accurate to ±0.1 K.

Materials Used

The methyl borate used was manufactured by the Aldrich Chemical Co., Inc., and was received at a nominal 99% purity. Methyl alcohol was manufactured by MCB Manufacturing Chemists, Inc., and received at a certified minimum purity of 99.8% with water content less than 0.1%, and a recorded boiling point of 337.75 K (64.6 °C). Benzene was manufactured by Burdick and Jackson Laboratories, Inc., and was specified with a purity greater than 99.5% and boiling point between 353.15 and 354.15 K (80–81 °C).

Chemicals were further purified by simple distillation. In the case of the methyl borate several distillations were performed to achieve a purity in excess of 99.9%. Approximately 50% of the original batch was recovered in this fashion. The standard mannitol–phenolphthalein method of analysis (*2*) for boric acid using 0.1 N sodium hydroxide was used for the analysis of the methyl borate. Properties of these compounds compared with literature values are shown in Table I.

Method of Analysis

Mixture analyses were made by a combination of chemical analysis and physical property measurements. This method has previously been used for systems of this type and found to be satisfactory (*6*). The same procedure was used here and involves the mannitol–sodium hydroxide titration for the methyl borate and measurement of the solution refractive index and solution density. Refractive indices were measured with a Bausch and Lomb Model 33-45-03 refractometer capable of precision to ±0.000 03 RI unit. The sodium D line (λ = 5893 Å) at 278.15 ± 0.05 K was used. Densities were determined by means of a pycnometer with a nominal value of 10 mL, at 278.15 ± 0.05 K. The pycnometer was calibrated with deionized water, specific resistance approximately 450 000, and weighed to ±0.0001 g. Analyses of known mixtures showed

0021-9568/84/1729-0178$01.50/0 © 1984 American Chemical Society

Table I. Physical Property Data

compd	bp, K		refractive index (298.15 K) sodium D line		density (298.15 K), kg/m^3	
	this work	lit.	this work	lit.	this work	lit.
methyl borate	341.75 ± 0.1	341.85 (*3*)	1.3550		927.2	927.3 (*5*)
methyl alcohol	337.75 ± 0.1	337.66 (*4*)	1.3266	1.326 57 (*4*)	786.3	786.54 (*4*)
benzene	353.15 ± 0.1	353.25 (*4*)	1.4976	1.497 92 (*4*)	873.4	873.79 (*4*)

Table II. Experimental Equilibrium Data for Methyl Borate-Methyl Alcohol-Benzene

point	temp, K	mole fraction liquid			vapor			activity coeff		
		$(CH_3O)_3B$	CH_3OH	C_6H_6	$(CH_3O)_3B$	CH_3OH	C_6H_6	$(CH_3O)_3B$	CH_3OH	C_6H_6
1	329.6	0.169	0.615	0.216	0.214	0.580	0.206	1.896	1.306	2.098
2	329.0	0.183	0.785	0.032	0.356	0.605	0.039	2.975	1.091	2.733
3	329.3	0.359	0.367	0.274	0.299	0.536	0.165	1.260	2.048	1.342
4	330.6	0.079	0.810	0.111	0.186	0.642	0.172	3.391	1.052	3.315
5	330.7	0.082	0.871	0.047	0.229	0.691	0.080	4.006	1.049	3.601
6	329.0	0.299	0.672	0.029	0.409	0.563	0.028	2.088	1.187	2.262
7	328.9	0.246	0.598	0.156	0.302	0.560	0.138	1.891	1.337	2.005
8	330.1	0.310	0.317	0.373	0.252	0.525	0.223	1.191	2.244	1.296
9	330.2	0.252	0.341	0.407	0.213	0.535	0.252	1.231	2.108	1.337
10	330.5	0.233	0.298	0.469	0.190	0.537	0.273	1.179	2.407	1.240
11	331.7	0.203	0.178	0.619	0.150	0.532	0.318	1.022	3.780	1.047
12	331.1	0.422	0.163	0.415	0.298	0.490	0.212	0.995	3.906	1.066
13	331.4	0.461	0.139	0.400	0.344	0.455	0.201	1.041	4.194	1.042
14	333.6	0.554	0.111	0.335	0.401	0.430	0.169	0.930	4.535	0.967
15	330.5	0.574	0.197	0.229	0.400	0.482	0.118	1.005	3.262	1.093
16	335.2	0.678	0.105	0.217	0.510	0.376	0.114	0.911	3.945	0.943
17	334.7	0.737	0.090	0.173	0.561	0.347	0.092	0.940	4.340	0.978
18	336.6	0.757	0.093	0.150	0.608	0.317	0.075	0.925	3.558	0.867
19	328.2	0.266	0.699	0.035	0.391	0.576	0.033	2.314	1.208	2.253
20	331.4	0.064	0.265	0.671	0.054	0.582	0.364	1.163	2.829	1.120
21	330.7	0.096	0.368	0.536	0.087	0.581	0.332	1.300	2.085	1.308
22	332.0	0.107	0.194	0.699	0.080	0.556	0.364	1.015	3.597	1.055
23	332.5	0.010	0.876	0.114	0.028	0.740	0.232	3.742	1.040	4.044
24	331.6	0.021	0.834	0.154	0.051	0.699	0.250	3.358	1.069	3.544
25	330.0	0.100	0.706	0.194	0.162	0.614	0.224	2.378	1.183	2.504

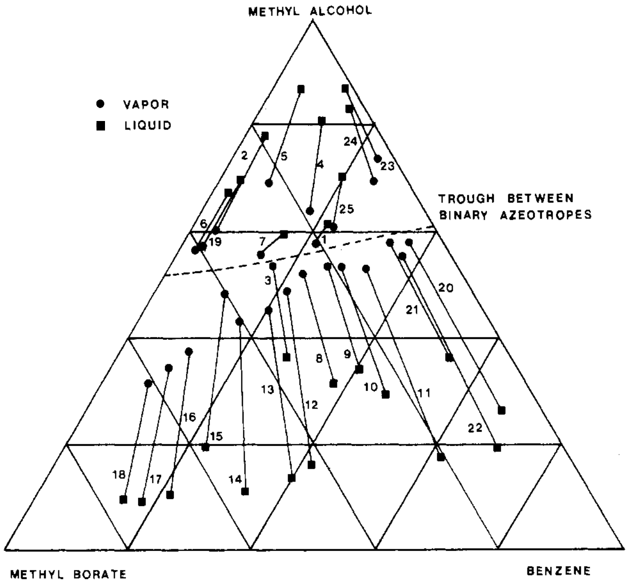

Figure 1. Equilibrium tie lines.

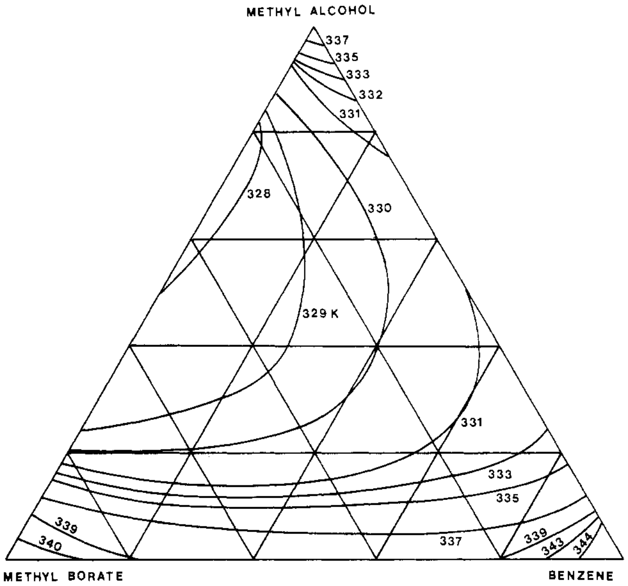

Figure 2. Isotherms of the liquid surface of the system methyl borate–methyl alcohol–benzene.

reproducibility to ±0.1% of the known values.

Experimental Results

Experimental data are tabulated in Table II and the tie lines are also shown in Figure 1. Estimated isotherms are shown for the liquid and vapor surfaces in Figures 2 and 3. The data along with the estimated tie lines do not indicate any maxima or minima within the interior of the phase surfaces; hence, the system does not contain a ternary azeotrope. For the liquid surface, a sharp temperature drop occurs from the methyl borate–benzene binary as small amounts of methyl alcohol are added. The drop is less severe at high methyl borate concentrations. The interior of the surface is nearly flat at points reasonably removed from the pure substances. The flat interior also rises rapidly as pure methyl alcohol is reached.

The vapor surface shows a trough with only slight curvature connecting the two binary azeotropes (methyl alcohol–benzene and methyl borate–methyl alcohol). The surfaces rising from the trough toward pure methyl alcohol and also toward the methyl borate–benzene binary show slightly outward curvature.

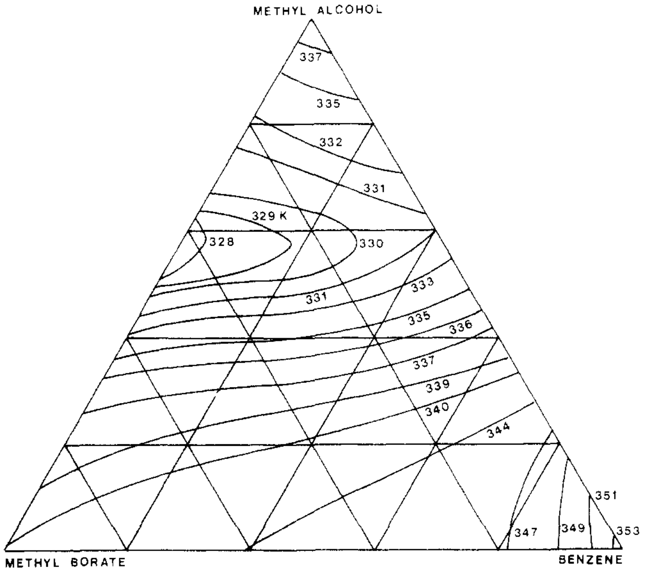

Figure 3. Isotherms of the vapor surface of the system methyl borate–methyl alcohol–benzene.

Table III. Binary Correlation Constants

system i-j	Margules constants		Wilson constants	
CH_3OH-$(CH_3O)_3B$	1.823 42	1.759 86	0.273 29	0.258 49
$(CH_3O)_3B$-C_6H_6	0	0	1	1
CH_3OH-C_6H_6	1.972 15	1.697 86	0.206 46	0.370 43

The shapes of the surfaces are quite similar to those found by Schindler et al. (*6*) for the methyl borate–methyl alcohol–carbon tetrachloride system.

Activity coefficients were calculated for each component by using the equation

$$\gamma_i = y_i P / x_i P^\circ \tag{1}$$

Estimations of the corrections caused by nonideality of the vapor phase were made by using the Soave modifications of the Redlich and Kwong equation with appropriate mixing rules. Values of the fugacity coefficients so calculated for both pure components and mixtures were between 0.99 and 1.00. Because of these small deviations and problems of estimating critical properties of the methyl borate and considering the precision of the other corrections, no vapor-phase corrections were made. The slight vapor-phase imperfections were absorbed into the liquid-phase activity coefficient as calculated by eq 1. Equations used for the vapor pressures of methyl alcohol and benzene were taken from ref *7* and for methyl borate the equation

$$\ln P^\circ = 18.6929 - 4106.92/T \tag{2}$$

was used where T is in Kelvin and P° in mmHg. This latter equation gives a slightly better representation of the experimental data than the previously reported equation of Plank and Christopher (*8*).

Data for the three binary systems which compose the ternary have been measured and reported previously (*8*–*10*) showing that methyl borate–benzene is an ideal system and the other two have minimum-boiling azeotropes. From the data for these systems binary constants were calculated for the Margules and Wilson equations (*11*). These constants are reported in Table III.

Ternary vapor compositions and equilibrium temperatures were estimated for the measured liquid compositions by using both the ternary form of the Margules (*1*) and Wilson equations.

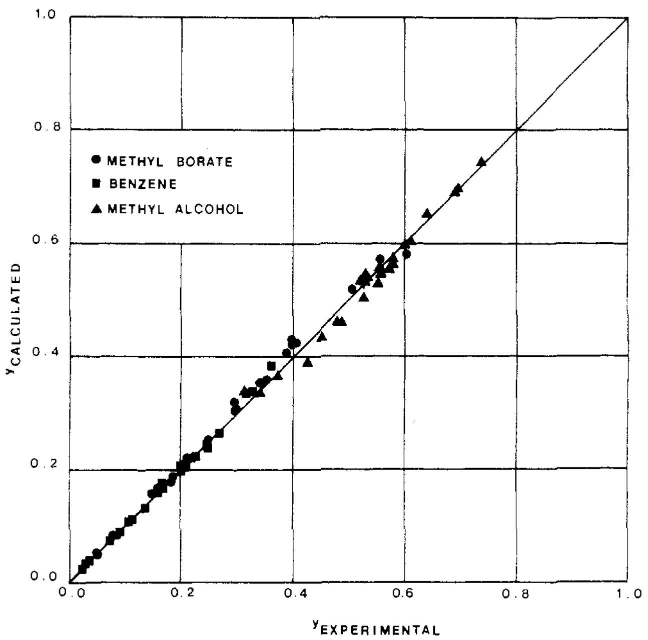

Figure 4. Comparison of calculated and experimental results using the ternary Margules equation.

The Wilson formulation employs only binary constants while the Margules format employs both the binary constants and a single ternary constant. The Margules ternary constant was evaluated for each ternary point and showed considerable variation. Because of this variation and the desire to evaluate predictions from only binary data the approximation for the ternary constant (from binary constants) given by Hala et al. (*1*) was used.

The Wilson expansion for $\ln \gamma_i$ is

$$\ln \gamma_i = 1 - \ln \left(\sum_j x_j \Lambda_{ij}\right) - \sum_j \left(\frac{x_k \Lambda_{ki}}{\sum_j x_j \Lambda_{kj}} \right) \tag{3}$$

and the Margules expansion is

$$\begin{aligned} \ln \gamma_i = {} & x_j^2[A_{ij} + 2x_i(A_{ji} - A_{ij})] + \\ & x_k^2[A_{ik} + 2x_i(A_{ki} - A_{ik})] + x_j x_k[A_{ji} + A_{ik} - A_{kj} + \\ & 2x_i(A_{ki} - A_{ik}) + 2x_k(A_{kj} - A_{jk}) - C(1 - 2x_i)] \end{aligned} \tag{4}$$

where the ternary constant C is approximated as

$$C = (1/2)(A_{ji} - A_{ij} + Ai_k - A_{ki} + A_{kj} - A_{jk}) \tag{5}$$

Values for $\ln \gamma$ for other constituents can be evaluated for eq 3 by changing subscripts i → j → k → i. Equations 3 and 4 were used separately to evaluate γ_i for the measured x_i. Then using eq 1, we solved for the value of y_i, iterating temperatures (which alter vapor-pressure values) until the summation of the y values equaled unity.

Results of the predictions of the vapor compositions indicated that the Margules equation gave a better overall representation of data. The Margules predictions had an overall average deviation of 1.13% (maximum 2.4%) while the Wilson equation had an overall deviation of 1.74% (maximum 5.7%). The average error of the estimation of any single component vapor composition was of the order 0.01 mole fraction with methyl alchol having the largest deviations. The largest deviations arise at low liquid methyl alchol concentrations where the vapor concentrations change markedly with small changes in liquid composition. Data comparing calculated and estimated values by the Margules equation are shown in Figure 4. The errors in the ternary estimation were of the same order of magnitude as found in the representation of the binary data and hence little accuracy is lost in going from binary to ternary estimations. Tabular comparisons of the estimations and computer programs for the various calculations are given by Münster (*12*).

Glossary

Λ_{ij}	constant in Wilson equation
A_{ij}	binary constant in Margules equation
C	ternary constant in Margules equation
P	total pressure
P°	vapor pressure
x	mole fraction, liquid
y	mole fraction, vapor
γ	activity coefficient

Registry No. $(CH_3O)_3B$, 121-43-7; CH_3OH, 67-56-1; C_6H_6, 71-43-2.

Literature Cited

(1) Hala, E.; Pick, J.; Fried, V.; Vilim, O. "Vapor-Liquid Equilibrium", 2nd English ed.; Pergamon Press: Oxford, 1967; p 305-6.
(2) Kolthoff, I. M.; Sandell, E. B. "Textbook of Quantitative Inorganic Analysis", 3rd ed.; Macmillan: London, 1952; p 534-5.
(3) Lange, N. A. "Handbook of Chemistry", 11th ed.; Handbook Publishing: Sandusky, OH, 1973.
(4) API Research Project 44 Tables; Thermodynamics Research Center Texas A&M University: College Station, TX, 1977.
(5) Christopher, P. M.; Washington, H. W. *J. Chem. Eng. Data* **1969**, *14*, 437.
(6) Schindler, L. E.; Plank, C. A.; Christopher, P. M.; Laukhuf, W. L. S. *J. Chem. Eng. Data* **1977**, *22*, 294.
(7) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. "The Properties of Gases and Liquids", 3rd ed.; McGraw-Hill: New York, 1977; pp 634-49.
(8) Plank, C. A.; Christopher, P. M. *J. Chem. Eng. Data* **1976**, *21*, 211.
(9) Serafimov, L. A.; Tyunikov, J. D.; Rumyantser, P. G.; Lvov, S. V. *Russ. J. Phys. Chem.* (*Engl. Transl.*) **1964**, *38*, 724.
(10) Nagata, I. *J. Phys. Chem.* **1969**, *14*, 418-20.
(11) Smith, J. M.; Van Ness, H. C. "Introduction to Chemical Engineering Thermodynamics", 3rd ed.; McGraw-Hill: New York, 1975; p 333-5.
(12) Münster, N. Master of Engineering Thesis, University of Louisville, Louisville, KY, 1983.

Received for review May 18, 1983. Accepted August 17, 1983.

Excess Thermodynamic Functions for Ternary Systems. 10. H^E and S^E for Ethanol/Chloroform/1,4-Dioxane at 50 °C

Mark Roach and Hendrick C. Van Ness*

Chemical and Environmental Engineering Department, Rensselaer Polytechnic Institute, Troy, New York 12181

Heat-of-mixing data for the ternary liquid system ethanol/chloroform/1,4-dioxane at 50 °C are reported, along with data for the constituent binaries. A correlation of these data, together with a similar correlation for G^E, allows calculation of S^E values.

We report heat-of-mixing data at 50 °C for the ethanol (1)/chloroform (2)/1,4-dioxane (3) system. Experimental values are presented for the full composition range of each constituent binary liquid system and for nine runs with ternary liquid mixtures formed by addition of a pure species to a mixture of the other two. The apparatus is essentially that of Winterhalter and Van Ness (*1*).

Reagent-quality ethanol was supplied by U.S. Industrial Chemicals and chromatoquality chloroform and dioxane came from Matheson Coleman and Bell. All were used as received with minimum indicated purity of 99.9 mol %.

Results and Correlations

Tables I-III give experimental values of H^E for the three constituent binary systems, and Table IV shows the data for ternary mixtures. These data, like the data for G^E reported earlier (*2*), are well correlated by equations of the form

$$M^E_{ij}/RT = [A_{ji}x_i + A_{ij}x_j - (D_{ji}x_i + D_{ij}x_j)x_ix_j + (E_{ji}x_i + E_{ij}x_j)(x_ix_j)^2]x_ix_j \quad (1)$$

$$M^E_{123}/RT = M^E_{12}/RT + M^E_{13}/RT + M^E_{23}/RT + x_1x_2x_3C \quad (2)$$

where

$$C = C_0 + C_1x_1 + C_2x_2 + C_3x_1^2 + C_4x_2^2 + C_5x_1x_2 \quad (3)$$

Table I. H^E-x Data for Ethanol (1)/Chloroform (2) at 50 °C

x_1	x_2	H^E, J mol^{-1}	x_1	x_2	H^E, J mol^{-1}
0.0288	0.9712	254.1	0.5985	0.4015	−3.7
0.0560	0.9440	430.4	0.6165	0.3836	−46.2
0.1125	0.8875	645.7	0.6316	0.3685	−85.1
0.1587	0.8413	719.9	0.6644	0.3356	−159.0
0.2191	0.7809	734.1	0.7156	0.2845	−262.2
0.2457	0.7543	719.7	0.7625	0.2375	−330.9
0.3144	0.6856	641.7	0.8173	0.1827	−369.4
0.3586	0.6414	567.2	0.8558	0.1442	−361.9
0.4017	0.5983	481.1	0.9006	0.0994	−309.7
0.4437	0.5563	386.6	0.9238	0.0762	−262.4
0.4960	0.5040	259.0	0.9483	0.0517	−196.1
0.5216	0.4784	195.7	0.9681	0.0319	−130.3
0.5481	0.4520	126.0	0.9893	0.0107	−47.8
0.5690	0.4310	73.8			

Table II. H^E-x Data for Ethanol (1)/1,4-Dioxane (3) at 50 °C

x_1	x_3	H^E, J mol^{-1}	x_1	x_3	H^E, J mol^{-1}
0.0093	0.9907	0 63.2	0.5383	0.4617	1602.0
0.0292	0.9708	1192.2	0.5651	0.4349	1586.4
0.0520	0.9480	333.1	0.5878	0.4122	1564.6
0.0758	0.9242	469.8	0.6215	0.3785	1524.2
0.1006	0.8994	607.9	0.6243	0.3757	1518.2
0.1397	0.8603	799.3	0.6743	0.3257	1430.1
0.1845	0.8155	995.4	0.7758	0.2242	1152.0
0.2316	0.7684	1168.1	0.8211	0.1789	983.4
0.2856	0.7144	1331.0	0.8631	0.1369	799.4
0.3364	0.6636	1450.1	0.9094	0.0906	566.1
0.3890	0.6110	1536.9	0.9481	0.0519	343.2
0.4380	0.5620	1587.6	0.9721	0.0279	191.2
0.4859	0.5141	1608.9	0.9893	0.0107	75.6

Heat-of-mixing data for the three binary systems are well correlated by eq 1 ($M^E_{ij} \equiv H^E_{ij}$) with the parameters listed in Table V. Combination of these parameters with the corresponding parameters for G^E_{ij} (*2*) in accord with the equation

0021-9568/84/1729-0181$01.50/0