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Vapor-Liquid Equilibrium of the System Methanol + Benzene + Cyclohexane at 760 mmHg

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Vapor-liquid equilibrium data for the system methanol + benzene + cyclohexane have been determined at 760 mmHg, and the results are compared with those calculated by the group contribution methods ASOG-KT and UNIFAC and the Wilson, NRTL, LEMF, and UNIQUAC equations (with correlation parameters calculated from experimental vapor-liquid equilibrium data for the corresponding binary systems).

Introduction

Rectification is one of the most important separation processes used by the chemical industry. For the design of rectifying columns, quantitative information is required concerning the vapor-liquid equilibria of the systems whose components are to be separated. Since the experimental determination of the vapor-liquid equilibria of multicomponent systems is a lengthy and often a costly process, various methods of prediction have been developed.

This article reports experimental vapor-liquid equilibrium data for the system methanol + benzene + cyclohexane at 760 mmHg and compares these data with values calculated by the ASOG-KT (*1*) and UNIFAC (*2*, *3*) methods and the Wilson (*4*), NRTL (*5*), LEMF (*6*), and modified UNIQUAC (*7*) equations. In all calculations, the nonideal nature of both phases was taken into account, the method of Hayden and O'Connell (*8*) being used to calculate the second virial coefficient and hence the fugacity of the vapor phase.

Experimental Section

Experimental equilibrium data for the ternary system were determined with Merck chromatography-grade products. Their purity was checked on the basis of their refractive indices and densities at 25 °C and their boiling points at 760 mmHg (Table I).

All experiments were carried out under an atmosphere of argon so as to prevent compounds from taking up water from the environment. Equilibrium data were obtained with an Othmer ebulliometer recycling both phases, as modified by Ocón and Espantoso (*9*). The boiling points of the mixtures were measured with a set of Siebert & Kühn mercury thermometers with a precision of ±0.03 °C. Pressure was kept at 760 ± 0.1 mmHg by introducing argon to make up for the pressure difference with respect to the pressure in the laboratory. Each experiment was continued for 1 h after the boiling point had become stable. The estimated precision of the equilibrium mixture composition measurements was ±0.001 mole fraction for the liquid phase and ±0.005 mole fraction for the vapor phase. The estimated uncertainties in the equilibrium temperature and pressure were ±0.01 °C and 0.5 mmHg, respectively.

Analysis of the liquid and vapor phases was performed by measuring densities and refractive indices at 25 °C and interpolating in previously determined refractive-index-composition and density-composition charts (*10*). The use of this analytical method prevented the experimental determination of VLE data for low concentrations of benzene, since the system methanol + benzene + cyclohexane is immiscible in this region at 25 °C.

Table I. Physical Properties of Pure Components

property	exptl data	lit. data	ref
Methanol			
density at 25 °C, g cm^{-3}	0.7864	0.78661	10
		0.78664	16
refractive index at 25 °C	1.32713	1.3261	10
		1.32652	16
boiling point at 760 mmHg, °C	64.57	64.65	17
		64.70	16
Benzene			
density of 25 °C, g cm^{-3}	0.8734	0.87359	18
		0.87370	16
refractive index at 25 °C	1.4967	1.49792	16
		1.497	19
boiling point at 760 mmHg, °C	80.11	80.09	19
		80.10	16
Cyclohexane			
density at 25 °C, g cm^{-3}	0.7738	0.77383	20
		0.77389	16
refractive index at 25 °C	1.4233	1.4233	21
		1.42354	16
boiling point at 760 mmHg, °C	80.66	80.7	13
		80.72	16

Table II presents the vapor-liquid equilibrium data measured experimentally, and in Figure 1, their distribution in the composition triangle may be readily appreciated. Each equilibrium composition is depicted in Figure 1 by an arrow, with the flight end representing the composition of the liquid phase and the arrowhead that of the vapor phase. Figure 2 shows equilibrium isotherms on the liquid-phase composition diagram obtained from the experimental data by graphical interpolation. The dashed curve in Figures 1 and 2 is the binodal curve at 25 °C determined by Arce et al. (*10*).

Determination of Correlation Parameters

Correlation parameters for the Wilson, NRTL, LEMF, and UNIQUAC equations were determined from published vapor-liquid equilibrium data for the binary systems methanol + benzene (*11*), methanol + cyclohexane (*12*), and benzene + cyclohexane (*13*). All the data used passed the consistency test of Fredenslund et al. (*14*), and the correlation parameters were optimized by using the maximum-likelihood-based algorithm of Prausnitz et al. (*15*), which minimizes the objective function

$$S = \sum_i \left(\frac{(P_i^c - P_i^e)^2}{\sigma_P{}^2} + \frac{(T_i^c - T_i^e)^2}{\sigma_T{}^2} + \frac{(x_{1i}^c - x_{1i}^e)^2}{\sigma_x{}^2} + \frac{(y_{1i}^c - y_{1i}^e)^2}{\sigma_y{}^2} \right)$$

where the superscripts c and e indicate calculated and experimental values, respectively; the σ^2 are the estimated variances of the corresponding variables; and the sum is taken over all M experimental data. The standard deviations assumed were

$$\sigma_P = 0.5 \text{ mmHg} \qquad \sigma_T = 0.1 \text{ °C}$$
$$\sigma_x = 0.001 \text{ mole fraction} \qquad \sigma_y = 0.005 \text{ mole fraction}$$

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Table II. Experimental Liquid-Vapor Equilibrium Temperatures and Compositions of the Mixtures Methanol + Benzene + Cyclohexane at 760 mmHg

run	temp, °C	liquid phase, mole fraction methanol	liquid phase, mole fraction benzene	vapor phase, mole fraction methanol	vapor phase, mole fraction benzene
1	58.95	0.917	0.063	0.778	0.130
2	56.75	0.836	0.125	0.656	0.213
3	56.95	0.764	0.198	0.638	0.267
4	56.80	0.694	0.273	0.610	0.310
5	56.90	0.606	0.354	0.573	0.327
6	56.90	0.519	0.434	0.583	0.346
7	57.15	0.427	0.520	0.579	0.359
8	59.70	0.116	0.250	0.494	0.155
9	54.70	0.194	0.238	0.552	0.135
10	54.60	0.266	0.228	0.561	0.128
11	54.60	0.380	0.214	0.565	0.140
12	54.80	0.460	0.206	0.559	0.149
13	54.80	0.532	0.190	0.562	0.151
14	54.80	0.597	0.176	0.570	0.156
15	54.80	0.651	0.160	0.564	0.157
16	55.00	0.707	0.146	0.578	0.164
17	55.05	0.737	0.129	0.608	0.154
18	55.15	0.764	0.115	0.616	0.146
19	55.25	0.813	0.084	0.615	0.118
20	55.40	0.736	0.161	0.599	0.194
21	55.80	0.650	0.247	0.577	0.248
22	56.10	0.574	0.323	0.569	0.278
23	56.35	0.489	0.400	0.582	0.279
24	56.70	0.390	0.483	0.560	0.317
25	57.20	0.301	0.559	0.543	0.334
26	57.50	0.307	0.584	0.541	0.360
27	57.50	0.302	0.620	0.546	0.371
28	59.10	0.250	0.700	0.528	0.412
29	61.80	0.148	0.794	0.482	0.465
30	61.80	0.112	0.534	0.415	0.332
31	55.70	0.139	0.243	0.548	0.140
32	55.00	0.166	0.210	0.549	0.119
33	55.70	0.142	0.240	0.554	0.132
34	55.10	0.272	0.319	0.551	0.190
35	54.90	0.261	0.293	0.549	0.171
36	55.00	0.356	0.275	0.556	0.177
37	54.90	0.465	0.240	0.553	0.172
38	54.90	0.530	0.225	0.561	0.178
39	55.30	0.531	0.265	0.558	0.214
40	55.70	0.481	0.342	0.554	0.257
41	56.10	0.411	0.421	0.546	0.283
42	56.30	0.331	0.494	0.544	0.302
43	56.90	0.240	0.608	0.531	0.343
44	60.50	0.167	0.686	0.478	0.405
45	63.30	0.101	0.774	0.425	0.470
46	56.95	0.160	0.437	0.511	0.243
47	55.30	0.294	0.382	0.545	0.221
48	55.35	0.404	0.339	0.548	0.224
49	55.90	0.322	0.446	0.541	0.269
50	56.80	0.221	0.553	0.542	0.297
51	61.30	0.147	0.629	0.443	0.382
52	56.70	0.150	0.528	0.472	0.315
53	55.70	0.183	0.427	0.526	0.228
54	55.90	0.273	0.457	0.535	0.264
55	78.10	0.013	0.949	0.024	0.924
56	78.36	0.009	0.897	0.004	0.872
57	75.67	0.016	0.815	0.080	0.737
58	74.25	0.014	0.601	0.076	0.546
59	68.24	0.027	0.506	0.221	0.399
60	68.80	0.016	0.431	0.207	0.340
61	70.20	0.005	0.368	0.178	0.319
62	71.35	0.010	0.300	0.170	0.265
63	67.43	0.018	0.261	0.275	0.216
64	71.25	0.021	0.675	0.165	0.548
65	61.00	0.090	0.453	0.434	0.281
66	59.90	0.084	0.385	0.473	0.228
67	58.85	0.080	0.320	0.504	0.187
68	62.20	0.061	0.592	0.394	0.366

The values of r, q, and q' used in the UNIQUAC equation were those proposed by Prausnitz et al. (*15*), and the values of the NRTL parameters considered were those proposed by

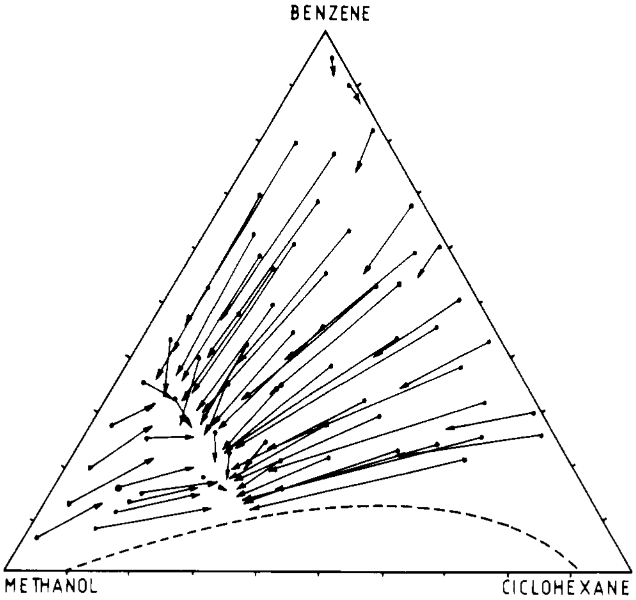

Figure 1. Composition diagram for the mixture methanol + benzene + cyclohexane. Flight ends of arrows indicate equilibrium concentrations of the liquid phase at 760 mmHg and the arrowheads the corresponding vapor-phase compositions.

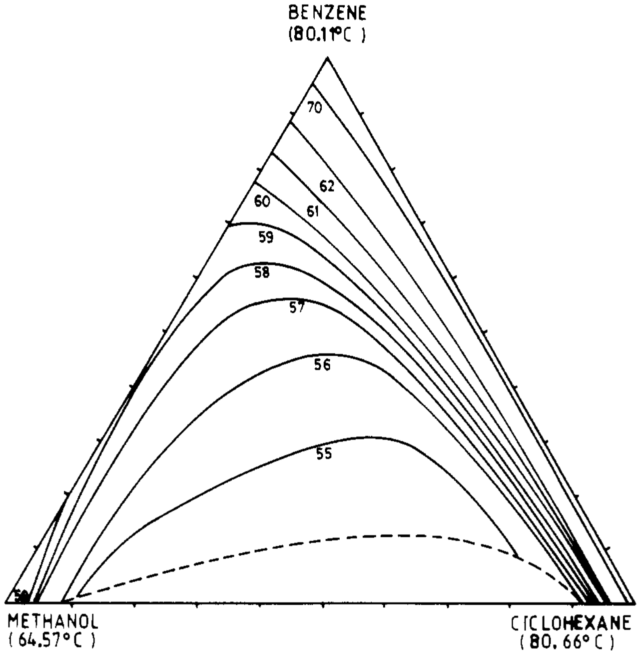

Figure 2. Composition diagram for the liquid phase of the mixture methanol + benzene + cyclohexane, showing constant boiling temperature (°C) contours at 760 mmHg.

Table III. Optimized Correlation Parameters for the Binary Systems, with the Corresponding Minimum of the Objective Function

eq	parameter	methanol + benzene	methanol + cyclohexane	benzene + cyclohexane
Wilson	$\Delta\lambda_{12}$	1762.19	2765.18	130.05
	$\Delta\lambda_{21}$	180.81	783.88	132.93
	S	141.65	359.03	13.72
NRTL	Δg_{12}	755.99	1657.76	353.02
	Δg_{21}	1123.74	1690.45	-87.71
	S	124.29	1712.79	13.43
LEMF	Δg_{12}	529.64	575.91	-663.30
	Δg_{21}	403.41	559.85	461.01
	S	108.27	488.39	14.07
UNIQUAC	ΔU_{12}	-123.69	5.94	22.71
	ΔU_{21}	935.05	2574.91	74.16
	S	151.16	449.83	13.49

Table IV. Root Mean Square (RMS) Deviations between the Experimental Temperatures and Vapor-Phase Compositions of the Binary Mixtures and Those Calculated by the ASOG-KT and UNIFAC Methods

	ASOG-KT		UNIFAC	
system	RMS t, °C	RMS y, mole fraction	RMS t, °C	RMS y, mole fraction
methanol + benzene	0.2833	0.0133	0.6442	0.0179
methanol + cyclohexane	0.4194	0.0336	0.5773	0.0292
benzene + cyclohexane	0.1655	0.0020	0.0812	0.0026

Table V. Root Mean Square (RMS) Deviations between the Experimental Temperatures and Vapor-Phase Compositions of the Ternary Mixture Methanol + Benzene + Cyclohexane and Those Calculated by Various Methods

		RMS vapor-phase, mole fraction		
method	RMS t, °C	methanol	benzene	cyclohexane
UNIFAC	1.61	0.0468	0.0338	0.0197
ASOG-KT	1.29	0.0403	0.0280	0.0174
NRTL	1.56	0.0446	0.0310	0.0200
LEMF	1.85	0.0493	0.0358	0.0207
UNIQUAC	1.61	0.0478	0.0337	0.0198
Wilson	1.68	0.0509	0.0351	0.0216

Renon and Prausnitz (*5*). Table III lists the optimized correlation parameters and the corresponding value of the objective function for each of the three binary systems and each of the four equations.

The excessively large value of the objective function obtained for the system methanol + cyclohexane with the NRTL equation may be due to an unfortunate choice of α, since a much better result is achieved by the LEMF equation, in which a value of $\alpha = -1.0$ was used regardless of the kind of system.

Prediction of the Vapor-Liquid Equilibria of the Binary Systems

The vapor-liquid equilibria of the binary systems methanol + benzene, methanol + cyclohexane, and benzene + cyclohexane were predicted by the ASOG-KT and UNIFAC methods. The group interaction parameters a_{nm} used for the UNIFAC method were those published by Gmehling et al. (*3*), and the ASOG-KT group parameters m_{kl} and n_{kl} were those proposed by Kojima and Tochigi (*1*).

The UNIFAC predictions for the system methanol + cyclohexane, which exhibit a maximum and a minimum in the immiscible region of the equilibrium diagram, have been corrected by drawing a straight line between the points of mutual solubility.

Table IV lists the root mean square deviations of the calculated temperatures and vapor-phase compositions from the experimental data.

Prediction of the Vapor-Liquid Equilibria of the Ternary System

Vapor-liquid equilibria for the ternary system methanol + benzene + cyclohexane were calculated by the ASOG-KT and UNIFAC methods and by using the Wilson, NRTL, LEMF, and UNIQUAC equations. Table V lists the root mean square deviations of the calculated temperatures and vapor-phase compositions from the experimental data. The smallest deviations of both temperature and composition were achieved by the ASOG-KT method.

The UNIFAC predictions for this ternary system deviated from the experimental results more widely than for other ternary systems that we have studied. This is probably because the calculations for the ternary system involve the use of the parameters employed for the binary system methanol + cyclohexane, which, as seen above, lead to errors. In the case of the ternary system, these errors cannot be corrected a posteriori as was done for the binary system.

Although no ternary azeotrope was detected experimentally, the possibility of its existence in the experimentally inaccessible immiscible region led to our seeking it by theoretical means. However, none of the prediction methods discovered any such ternary azeotrope.

Conclusions

Experimental vapor-liquid equilibrium data were determined at 760 mmHg for methanol + benzene + cyclohexane mixtures corresponding to almost all areas of the ternary composition chart except the relatively small immiscible region coinciding with low benzene concentrations.

In order to determine the correlation parameters necessary for predicting the vapor-liquid equilibrium behavior of the ternary system, the Wilson, NRTL, LEMF, and UNIQUAC equations were fitted to published experimental vapor-liquid equilibrium data for the binary systems methanol + benzene, methanol + cyclohexane, and benzene + cyclohexane that had passed Fredenslund's consistency test.

The behavior of the binary systems was likewise predicted by the ASOG-KT and UNIFAC methods. Comparison of the results with the experimental data failed to identify either method as clearly better than the other.

When the vapor-liquid equilibrium behavior of the ternary system methanol + benzene + cyclohexane was predicted by the ASOG-KT and UNIFAC methods and the Wilson, NRTL, LEMF, and UNIQUAC equations, the ASOG-KT method achieved the smallest deviations from the experimental data.

For the system studied, only the LEMF equation proved better than the NRTL equation for correlation of the data for the system methanol + cyclohexane, for which a very large value of the objective function was obtained with the NRTL equation.

List of Symbols

Δg_{12}, Δg_{21}	NRTL parameters (cal mol^{-1})
M	number of experimental points
P	pressure (mmHg)
q	UNIQUAC parameter
q'	parameter of the UNIQUAC equation for water and alcohols
r	UNIQUAC parameter
S	objective function
T	absolute temperature (K)
Δu_{12}, Δu_{21}	UNIQUAC parameters (cal mol^{-1})
x	liquid-phase mole fraction
y	vapor-phase mole fraction

Greek Letters

α	NRTL parameter
$\Delta\lambda_{12}$, $\Delta\lambda_{21}$	Wilson parameters (cal mol^{-1})
σ^2	variance

Superscripts

c	calculated value
e	experimental value

Subscripts

i	ith component

Literature Cited

(1) Kojima, K.; Tochigi, K. *Prediction of Vapor-Liquid Equilibria by the ASOG Method*; Elsevier: Tokyo, 1979.

(2) Fredenslund, Aa.; Jones, R. L.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 1086.
(3) Gmehling, J.; Rasmussen, P.; Fredenslund, Aa. *Ind. Eng. Chem. Process Des. Dev.* **1982**, *21*, 118.
(4) Wilson, J. M. *J. Am. Chem. Soc.* **1964**, *86*, 127.
(5) Renon, H.; Prausnitz, J. M. *AIChE J.* **1968**, *14*, 135.
(6) Marina, J. M.; Tassios, D. *Ind. Eng. Chem. Process Des. Dev.* **1973**, *12*, 67.
(7) Anderson, T.; Prausnitz, J. M. *Ind. Eng. Chem. Process Des. Dev.* **1978**, *17*, 552.
(8) Hayden, J. G.; O'Connell, J. P. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209.
(9) Ocón, J.; Espantoso, J. *An. Quim.* **1956**, *54B*, 413.
(10) Arce, A.; Blanco, A.; Quintela, M. D.; Antorrena, G. *An. Quim.* **1980**, *76*, 405.
(11) Nagata, I. *J. Chem. Eng. Data* **1969**, *14*, 418.
(12) Marinichev, A. N.; Susarev, M. P. *Zh. Prikl. Khim. (Leningrad)* **1965**, *38*(7), 1619.
(13) Nagata, I. *J. Chem. Eng. Data* **1962**, *7*, 461.
(14) Fredenslund, Aa.; Gmehling, J.; Rasmussen, P. *Vapor-Liquid Equilibria Using UNIFAC*; Elsevier: Amsterdam, 1977.
(15) Prausnitz, J. M.; Anderson, T.; Grens, E.; Eckert, C.; Hsieh, R.; O'Connel, J. P. *Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria*; Prentice-Hall: Englewood Cliffs, NJ, 1980.
(16) Riddick, J. A.; Bunger, W. B. *Techniques of Chemistry, Organic Solvents*, 3rd ed.; Wiley: New York, 1970; Vol. II.
(17) Timmermans, J. *Physico-Chemical Constants of Pure Organic Compounds*; Elsevier: Amsterdam, 1965; Vol II.
(18) Brown, I.; Edwald, A. H. *Aust. J. Sci. Res., Ser. A* **1951**, *4*, 198.
(19) Mann, R. S.; Shemilt, L. W.; Waldichuck, M. *J. Chem. Eng. Data* **1963**, *8*, 502.
(20) Brown, I.; Edwald, A. H. *Aust. J. Sci. Res., Ser. A* **1950**, *3*, 306.
(21) Brown, I. *Aust. J. Sci. Res., Ser. A* **1952**, *5*, 530.

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Excess Volumes for Ternary Mixtures Containing 1,1,1-Trichloroethane + *n*-Hexane with 1-Propanol, 1-Butanol, and 1-Pentanol, at 303.15 K

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Excess volumes of three ternary mixtures were measured at 303.15 K. The mixtures included 1,1,1-trichloroethane and *n*-hexane as common components. 1-Propanol, 1-butanol, and 1-pentanol were noncommon components. Excess volumes are positive over the entire range of composition in the three mixtures. The positive excess volume has been attributed to the dominant nature of the structure-breaking effect of the components. The experimental results were also compared with those predicted by empirical equations (*1*).

Introduction

It is observed from a survey of the literature that excess thermodynamic properties of ternary mixtures have been measured to a limited extent. Further, it is found that no data have been collected for ternary mixtures that include halogenated hydrocarbons and hydrocarbons as common components. Hence, we report here new experimental data, at 303.15 K, for excess volumes of three ternary mixtures. The mixtures included 1,1,1-trichloroethane and hexane as common components and 1-propanol, 1-butanol, and 1-pentanol as noncommon components. The measured excess volumes have been compared with those predicted from binary data with use of semiempirical equations (*1*).

Experimental Section

The ternary excess volumes were measured by a single component per loading dilatometer described by Naidu and Naidu (*2*). The mixing cell contained three bulbs of different capacities. Mercury was used in the bottom to separate three components. One of the three bulbs was fitted with a capillary (i.d., 1.0 mm), and the other two were fitted with ground-glass stoppers. The excess volumes measured were accurate to ±0.003 cm^3 mol^{-1}.

Table I. Densities of Pure Components at 303.15 K

compound	densities, g/cm^3 experimental	literature[5]
1,1,1-trichloroethane	1.32102	1.32096
1-propanol	0.79571	0.79567
1-butanol	0.80194	0.80206
1-pentanol	0.80752	0.80764
n-hexane	0.65063	0.65070

All the chemicals used were of analytical grade. The alcohols were further purified by the methods described by Rao and Naidu (*3*). 1,1,1-Trichloroethane and *n*-hexane were purified by the methods described by Riddick and Bunger (*4*). The dried samples were distilled through a fractionating column. The purity of the samples was checked by comparing the measured densities with those reported in the literature (*5*) (Table I). The densities were measured by a bicapillary pycnometer that offered an accuracy of 3 parts in 10^5.

Results

The excess volume data for three ternary systems are given in Table II. The binary data for 1,1,1-trichloroethane with 1-alkanols and 1,1,1-trichloroethane with *n*-hexane were taken from the literature (*6*, *7*). The measured excess volume data for the binary systems of *n*-hexane with the three 1-alkanols are graphicly represented in Figure 1. The least-squares parameters for all these binary systems are given in Table III. The ternary excess volume data predicted on the basis of empirical equations proposed by Redlich-Kister, Kohler, and Tsao-Smith, are given in columns 3-5 of Table II.

The dependence of experimental ternary excess volumes V^E_{123}(exp) on composition is expressed by the polynomial

$$V^E_{123}(\text{exp}) = V^E_{123}(\text{b}) + X_1X_2X_3[A + BX_1(X_2 - X_3) + CX_1^2(X_2 - X_3)^2] \quad (1)$$

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