(3) Ohe, S. "Computer Aided Data Book of Vapor Pressure"; Data Book Publishing: Tokyo, 1976.
(4) Yen, L. C.; Woods, S. S. *AIChE J.* **1966**, *12*, 95.
(5) Wilson, G. M. *J. Am. Chem. Soc.* **1964**, *86*, 127.
(6) Abrams, D. S.; Prausnitz, J. M. *AIChE J.* **1975**, *21*, 116.
(7) Nelder, J. A.; Mead, R. *Comput. J.* **1965**, *7*, 308.
(8) Gmehling, J.; Onken, U. "Vapor-Liquid Equilibrium Data Collection"; DECHEMA: Frankfurt, 1977; Vol. 1, Part 1.
(9) Timmermanns, J. "Physico-Chemical Constants of Pure Organic Compounds"; Elsevier: Amsterdam, 1950.
(10) Weast, R. C. "Handbook of Chemistry and Physics", 53rd ed.; Chemical Rubber Publishing Co.: Cleveland, OH, 1972-1973.

Received for review June 23, 1982. Accepted May 12, 1983.

Supplementary Material Available: Complete tables of experimental and calculated VLE data of binary and two ternary systems (16 pages). Ordering information is given on any current masthead page.

Ternary System Methane–Carbon Dioxide–Hydrogen Sulfide. Excess Enthalpy Data by Flow Calorimetry

Alpha O. Barry, Serge C. Kaliaguine, and Rubens S. Ramalho*

Department of Chemical Engineering, Laval University, Ste-Foy, Quebec, Canada G1K 7P4

Excess enthalpy measurements for the ternary system methane–carbon dioxide–hydrogen sulfide in gaseous phase were performed utilizing an isothermal flow calorimeter. The investigation was conducted at three temperatures, 293.15, 305.15, and 313.15 K, and pressures of 0.507, 1.013, and 1.520 MPa (5, 10, and 15 atm, respectively). The determination of the excess enthalpies for the binary systems methane–carbon dioxide and methane–hydrogen sulfide has been the object of two previous articles. The binary interaction constants, k_{ij}, obtained for these binary systems by nonlinear regression, have been utilized as initial values for an analogous iteration procedure applied in the treatment of the experimental data obtained for the ternary system. Two series of binary interaction constants, k_{ij}, have been determined from the experimental data: coefficients k_{ij} independent of temperature and pressure, and k_{ij}'s adjusted as a function of temperature and pressure. A better prediction of the excess enthalpy experimental data was obtained from the latter series of binary interaction coefficients.

Introduction

A complete literature review of excess enthalpy measurements for binary systems in gaseous phase was presented in preceding articles (*1*, *2*). The importance of excess enthalpy data, from both the scientific point of view as well as that related to equipment design, was also discussed in these articles.

Experimental data of excess enthalpy for the binary systems methane–carbon dioxide (*1*) and methane–hydrogen sulfide (*2*) were reported. The binary interaction constants k_{ij} computed for optimal portrayal of the experimental data were also presented.

Following a logical sequence in our investigation program, this article presents excess enthalpy data for the ternary system methane–carbon dioxide–hydrogen sulfide.

The flow calorimeter utilized throughout this entire program possesses only two independent inlets for gaseous streams. Consequently, one series of cylinders containing a binary mixture of 86.8% methane and 13.2% hydrogen sulfide was prepared for this investigation. A second series of cylinders of 99.8% pure carbon dioxide, containing 100 ppm of CO, 50 ppm of H_2, 100 ppm of H_2O, and approximately 0.2% of N_2 as impurities, was utilized in conjunction with the series of cylinders of binary mixtures methane–hydrogen sulfide. The experimental measurements reported in this article encompass only excess enthalpy data within the range of ternary compositions obtained by mixing the gaseous contents of these two series of cylinders.

Experimental Method

A detailed description of the equipment and experimental method has been presented in previous articles (*1*–*5*). As indicated in the introductory section of this article, like in the case of the study of binary systems, two gaseous streams arrive independently at the calorimeter inlet, under temperature and pressure conditions T_1, P_1 and T_2, P_2, respectively. For the case of the ternary system methane–carbon dioxide–hydrogen sulfide, which is reported in this article, one of the gas streams is a binary mixture of methane and hydrogen sulfide. The choice of the percentages of 86.8% methane to 13.2% hydrogen sulfide was guided by the intention of utilizing a proportion within the range of typical compositions for natural gas.

The other stream is 99.8% pure carbon dioxide. These two gaseous streams arrive by independent lines to the calorimeter under temperature and pressure conditions which are nearly identical, i.e., $T_1 \approx T_2$ and $P_1 \approx P_2$. Then the two streams are mixed thoroughly. Since the mixture is endothermic, the process is accompanied by a temperature drop. To compensate for this temperature drop, a measured quantity of energy is supplied to the system by a power supply, so that the temperature of the exit gas mixture, T_0, at the calorimeter outlet is very nearly the same as the inlet temperatures (T_1, T_2) of the two entering gas streams.

The main objective of the investigation reported in this article is to verify the possibility of utilization of results obtained from the binary systems, in particular the binary interaction coefficients k_{ij}, for prediction of experimental data for the ternary system. In order to direct this study in a rational manner, the same nominal temperature and pressure conditions utilized in the study of the binary systems have been selected for the present study of the ternary system. The nominal temperatures were 293.15, 305.15, and 313.15 K. For each of these isotherms experiments were conducted at pressures of 0.507, 1.013, and 1.520 MPa (5, 10, and 15 atm, respectively).

Experimental Results

As previously found for the two binary systems methane–carbon dioxide (*1*) and methane–hydrogen sulfide (*2*), the pressure drops across the calorimeter, i.e., $\Delta P_1 = P_1 - P_0$ and $\Delta P_2 = P_2 - P_0$ are below 7×10^{-4} MPa, and therefore negligible. The temperature differences, i.e., $\Delta T_1 = T_1 - T_0$ and $\Delta T_2 = T_2 - T_0$, are below 0.05 K. Consequently, it is justifiable

0021-9568/83/1728-0375$01.50/0

to utilize mean values of the isothermal Joule–Thomson coefficients, $\bar{\phi}_A$, $\bar{\phi}_B$, and $\bar{\phi}_C$, and mean values of the molar heat capacities, $\bar{C}_{P,A}$, $\bar{C}_{P,B}$, and $\bar{C}_{P,C}$, for the pure compounds, i.e., methane, carbon dioxide, and hydrogen sulfide, respectively, in the application of eq 2-4 of ref *1*, for evaluation of the primary corrections. The excess enthalpies H_0^E are obtained from

$$H_0^E = \Delta H_m = Q/F + X_A(H_{A,1} - H_{A,0}) + X_B(H_{B,2} - H_{B,0}) + X_C(H_{C,1} - H_{C,0}) + (X_A + X_C)H_1^E{}_{(1,3)} - \Delta E_k \quad (1)$$

In eq 1 the term $H_1^E{}_{(1,3)}$ represents the heat of mixing for the binary system methane–hydrogen sulfide, for 86.8% of methane and 13.2% of hydrogen sulfide. This term $H_1^E{}_{(1,3)}$ was determined from the results reported in a previous article (*2*) for the outlet conditions T_0 and P_0. The terms X_A, X_B, and X_C represent the mole fractions of methane, carbon dioxide, and hydrogen sulfide in the ternary mixture. Furthermore, in eq 1

$$H_{A,1} - H_{A,0} = \int_{T_0}^{T_1} C_{P,A}\,dT + \int_{P_0}^{P_1} \phi_A\,dP \quad (2)$$

$$H_{B,2} - H_{B,0} = \int_{T_0}^{T_2} C_{P,B}\,dT + \int_{P_0}^{P_2} \phi_B\,dP \quad (3)$$

$$H_{C,1} - H_{C,0} = \int_{T_0}^{T_1} C_{P,C}\,dT + \int_{P_0}^{P_1} \phi_C\,dP \quad (4)$$

$$\Delta E_k = E_{k,A-B-C,0} - [X_B E_{k,B,2} + (X_A + X_C)E_{k,A-C,1}] \quad (5)$$

Utilizing the mean values for the isothermal Joule–Thomson coefficients and the molar heat capacities, eq 1 becomes

$$H_0^E = Q/F + X_A\bar{C}_{P,A}(T_1 - T_0) + X_B\bar{C}_{P,B}(T_2 - T_0) + X_C\bar{C}_{P,C}(T_1 - T_0) + X_A\bar{\phi}_A(P_1 - P_0) + X_B\bar{\phi}_B(P_2 - P_0) + X_C\bar{\phi}_C(P_1 - P_0) + (X_A + X_C)H_1^E{}_{(1,3)} - \Delta E_k \quad (6)$$

A second series of corrections, referred to as secondary corrections, are also required since the nominal conditions of temperature and pressure, T_n and P_n, are not always identical with the outlet conditions of the calorimeter, T_0 and P_0. These secondary corrections are performed by utilizing the following equation:

$$H_n^E = H_0^E + \int_{T_0}^{T_n} C_P^E\,dT + \int_{P_0}^{P_n} \phi^E\,dP \quad (7)$$

As in the case of the preceding articles (*1*, *2*), the determination of C_P^E and ϕ_E was made by application of the Benedict–Webb–Rubin equation of state (*6*). The analytical expressions for these quantities were presented in ref *1*.

The molar heat capacities for methane and carbon dioxide are those reported by Tester (*7*), and those for hydrogen sulfide were determined from the tables by Lee and Kesler (*8*).

The experimental results of the excess enthalpy for the ternary system methane–carbon dioxide–hydrogen sulfide are presented in Table I. Figures 1–3 present the same data in graphical form.

The contributions of the primary corrections upon the values of the excess enthalpies, H_0^E, and those of the secondary corrections upon H_n^E, have been expressed in the following manner:

for the primary corrections

$$100\left[\frac{H_0^E - Q/F - (X_A + X_C)H_1^E{}_{(1,3)}}{Q/F}\right]$$

for the secondary corrections

$$100\left[\frac{H_n^E - H_0^E}{H_n^E}\right]$$

The mean values of these two quantities for the whole network of experimental values are presented in Table II.

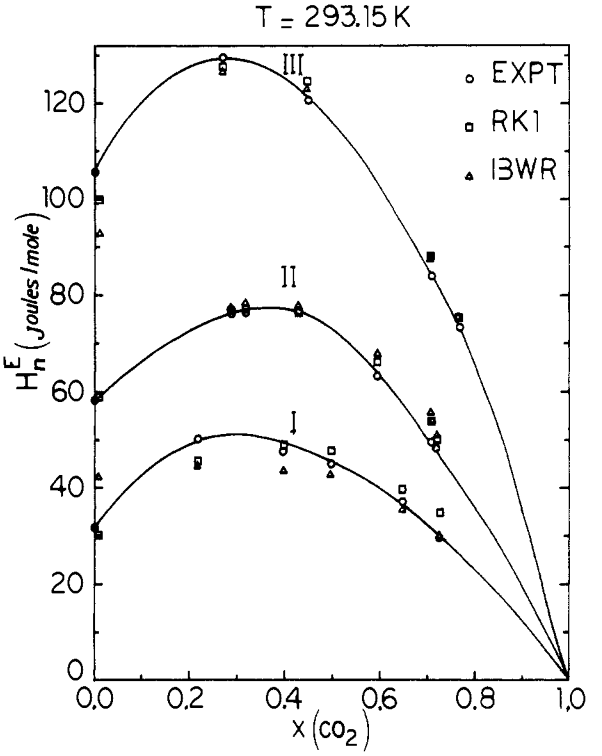

Figure 1. Excess enthalpies (J/mol) for the ternary system methane–carbon dioxide–hydrogen sulfide at 293.15 K: (I) 0.507, (II) 1.013, and (III) 1.520 MPa.

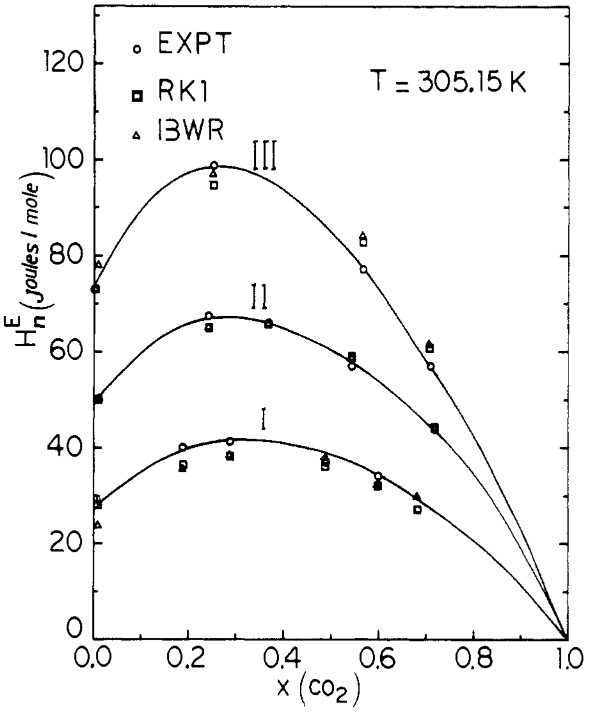

Figure 2. Excess enthalpies (J/mol) for the ternary system methane–carbon dioxide–hydrogen sulfide at 305.15 K: (I) 0.507, (II) 1.013, and (III) 1.520 MPa.

Corrections relative to the changes for the kinetic energy of the gas are negligible, being of the order of 10^{-6} J/mol.

Accuracy of the Experimental Results

The same technique utilized in the previous articles (*1*, *2*) was utilized for evaluation of errors. A summation of all experimental errors and those attributable to the primary and secondary corrections led to mean uncertainties of the order

Table I. Excess Enthalpies for the Ternary System Methane-Carbon Dioxide-Hydrogen Sulfide[a]

T_0, K	P_0, MPa	X_A	X_B	Q/F, J/mol	H_0^E, J/mol	H_n^E, J/mol			
						exptl	RK1	RK2	BWR
Nominal Conditions: T_n = 293.15; P_n = 0.507 MPa									
293.154	0.523	0.237	0.727	22.2	30.8	29.9	34.6	35.1	30.5
293.161	0.540	0.299	0.656	28.7	39.5	37.6	40.2	40.3	35.7
293.159	0.540	0.436	0.497	31.5	47.3	45.0	48.0	46.9	42.5
293.158	0.532	0.519	0.402	30.7	49.5	47.8	49.5	47.7	43.0
293.159	0.524	0.677	0.220	27.0	51.6	50.6	45.8	43.6	44.7
Nominal Conditions: T_n = 293.15 K; P_n = 1.013 MPa									
293.142	0.987	0.242	0.721	32.6	48.4	49.0	52.1	55.0	54.5
293.142	0.987	0.253	0.708	32.6	48.4	49.7	53.8	56.6	56.3
293.158	0.994	0.353	0.594	39.7	62.8	63.4	66.2	67.8	68.9
293.147	0.993	0.496	0.428	42.2	75.7	76.6	76.1	75.0	78.3
293.141	1.008	0.594	0.316	36.2	76.2	76.5	77.4	74.7	78.9
293.141	1.008	0.615	0.292	34.5	75.9	76.1	77.2	74.2	78.4
Nominal Conditions: T_n = 293.15 K; P_n = 1.529 MPa									
293.158	1.538	0.199	0.771	48.2	73.9	73.7	75.2	79.7	75.5
293.158	1.538	0.248	0.714	54.1	84.3	84.0	88.6	92.6	88.3
293.157	1.447	0.472	0.457	60.4	117.7	120.8	124.7	124.4	123.4
293.157	1.471	0.632	0.272	51.1	127.4	129.9	127.7	125.4	124.5
Nominal Conditions: T_n = 305.15 K; P_n = 0.507 MPa									
305.154	0.513	0.271	0.688	18.7	27.5	27.3	27.6	35.0	30.1
305.147	0.515	0.346	0.601	23.9	35.0	34.7	32.2	39.4	34.7
305.157	0.515	0.441	0.492	23.2	37.4	37.2	36.1	41.9	38.3
305.180	0.536	0.616	0.290	22.2	42.5	41.2	37.8	38.8	38.2
305.160	0.529	0.703	0.190	18.5	41.3	40.2	36.1	34.0	35.0
Nominal Conditions: T_n = 305.15 K; P_n = 1.013 MPa									
305.141	1.020	0.243	0.720	29.9	43.8	43.7	44.4	45.8	44.3
305.133	1.001	0.396	0.544	35.0	56.9	57.3	59.8	59.8	59.7
305.159	1.021	0.544	0.373	34.9	66.6	66.3	66.0	65.0	65.8
305.157	1.028	0.656	0.245	30.7	68.5	67.9	65.1	64.5	64.7
Nominal Conditions: T_n = 305.15 K; P_n = 1.520 MPa									
305.172	1.483	0.229	0.736	36.7	56.3	57.2	61.6	65.9	62.4
305.157	1.484	0.370	0.574	45.6	76.4	77.5	83.4	86.0	85.0
305.159	1.456	0.645	0.257	42.2	96.2	99.1	94.0	91.7	97.0
Nominal Conditions: T_n = 313.15 K; P_n = 0.507 MPa									
313.145	0.534	0.299	0.655	24.2	26.6	25.9	25.4	27.2	26.8
313.167	0.510	0.468	0.461	25.2	30.9	30.8	29.4	30.3	31.4
313.135	0.517	0.549	0.368	27.1	32.6	32.3	28.8	30.5	30.9
313.185	0.513	0.662	0.237	20.2	28.2	27.9	25.0	25.5	27.3
Nominal Conditions: T_n = 313.15 K; P_n = 1.013 MPa									
313.152	0.998	0.369	0.574	23.9	43.3	43.7	46.1	50.5	46.5
313.144	1.059	0.500	0.424	27.9	54.4	52.8	53.7	55.5	53.2
313.144	1.059	0.593	0.317	25.3	56.6	54.8	56.5	55.8	55.0
313.160	1.013	0.642	0.260	25.4	58.9	58.9	57.1	55.0	55.0
Nominal Conditions: T_n = 313.15 K; P_n = 1.520 MPa									
313.156	1.569	0.169	0.806	25.2	38.7	38.1	38.9	45.8	42.7
313.167	1.459	0.458	0.472	43.2	77.5	79.5	75.8	81.4	82.6
313.157	1.466	0.532	0.387	45.7	85.7	87.7	79.5	83.4	86.4
313.156	1.466	0.661	0.239	39.5	88.5	90.8	80.9	81.4	87.1

[a] Calculated values from equations of state utilized binary iteration coefficients k_{ij} adjusted as function of temperature and pressure.

Table II. Effect of the Primary and Secondary Corrections upon the Excess Enthalpies for the Ternary System Methane-Hydrogen Sulfide-Carbon Dioxide

T, K	293.15	305.15	313.15
$100[(H_0^E - Q/F - (X_A + X_C)H_1^E{}_{(1,3)})]/(Q/F)$	0.5	1.0	1.5
$100[(H_n^E - H_0^E)]/H_n^E]$	2.0	1.0	2.0

of 5% for the overall network of values for the excess enthalpies, H_n^E.

Comparison of Experimental Data with Predictions from Equations of State

Since experimental data of excess enthalpies for the ternary system methane-carbon dioxide-hydrogen sulfide were not available in the literature, the only possible comparison that could be done was with predictions based upon equations of state. For this purpose, we utilized the same equations of state previously employed (*1*, *2*): namely, the Redlich-Kwong equation (*9*), henceforth referred to as RK1; the Redlich-Kwong equation with Jacoby-Robinson modifications (*10*), henceforth referred to as RK2; and the Benedict-Webb-Rubin equation (*6*), henceforth referred to as BWR.

Equation of State of Redlich-Kwong (RK1). The network of RK1 equations for calculation of the theoretical values for the excess enthalpies is as follows:

$$P = \frac{RT}{V - b} - \frac{a}{T^{1/2}V(V + b)} \tag{8}$$

$$a_m = \sum_i \sum_j X_i X_j a_{ij} = X_A^2 a_{11} + X_B^2 a_{22} + X_C^2 a_{33} + 2X_A X_B a_{12} + 2X_A X_C a_{13} + 2X_B X_C a_{23} \tag{9}$$

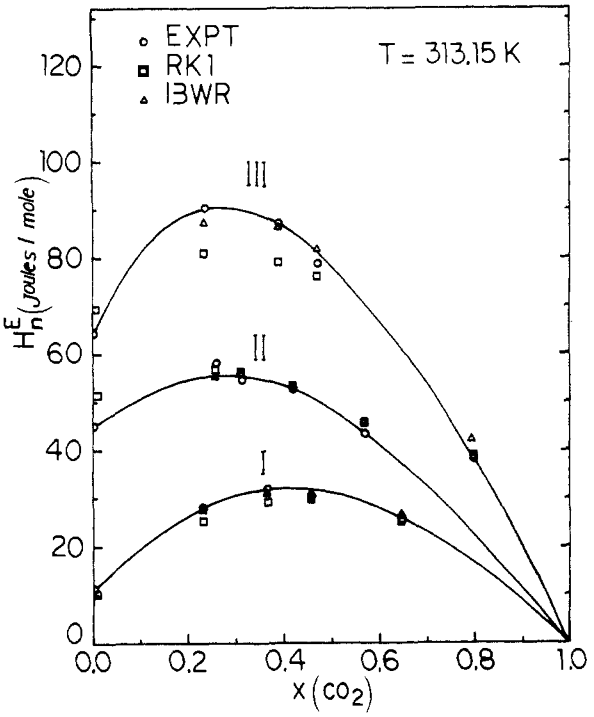

Figure 3. Excess enthalpies (J/mol) for the ternary system methane-carbon dioxide-hydrogen sulfide at 313.15 K: (I) 0.507, (II) 1.013, and (III) 1.520 MPa.

Table III. Binary Interaction Coefficients k_{ij} Obtained from the Experimental Values for the Excess Enthalpies in Table I[a]

systems	RK1	RK2	BWR
binary CH_4-CO_2, k_{12}	0.13	−0.24	0.013
binary CH_4-H_2S, k_{13}	0.27	0.30	0.13
ternary CH_4-CO_2, k_{12}	0.236	0.48	0.017
ternary CH_4-H_2S, k_{13}	0.40	0.66	0.187
ternary CO_2-H_2S, k_{23}	0.15	−2.61	0.30

[a] Coefficients k_{ij} independent of temperature and pressure.

Table IV. Comparison of Experimental Values of the Excess Enthalpies for the Ternary System Methane-Carbon Dioxide-Hydrogen Sulfide with Predictions Based upon Equations of State[a]

T, K	293.15	305.15	313.15
$100[(H_n{}^E{}_{\text{exptl}} - H_n{}^E{}_{\text{RK1}})/H_n{}^E{}_{\text{exptl}}]$	10.3	17.0	21.0
$100[(H_n{}^E{}_{\text{exptl}} - H_n{}^E{}_{\text{RK2}})/H_n{}^E{}_{\text{exptl}}]$	12.7	17.3	18.3
$100[(H_n{}^E{}_{\text{exptl}} - H_n{}^E{}_{\text{BWR}})/H_n{}^E{}_{\text{exptl}}]$	11.3	17.3	17.0

[a] Coefficients k_{ij} independent of temperature and pressure.

$$b_m = \sum_i X_i b_i = X_A b_1 + X_B b_2 + X_C b_3 \qquad (10)$$

where

$$a_{ij} = (\Omega_{ai} + \Omega_{aj}) R^2 T_{cij}{}^{2.5} / (2P_{cij}) \qquad (11)$$

$$T_{cij} = (1 - k_{ij})(T_{ci} T_{cj})^{1/2} \qquad (12)$$

$$P_{cij} = Z_{cij} R T_{cij} / V_{cij} \qquad (13)$$

$$Z_{cij} = 0.291 - 0.8(\omega_i + \omega_j)/2 \qquad (14)$$

$$V_{cij} = \{(V_{ci}{}^{1/3} + V_{cj}{}^{1/3})/2\}^3 \qquad (15)$$

$$a_{ii} = \Omega_{ai} R^2 T_{ci}{}^{2.5} / P_{ci} \qquad (16)$$

$$b_{ii} = \Omega_{bi} R T_{ci} / P_{ci} \qquad (17)$$

The enthalpies of the pure components, methane, carbon dioxide, and hydrogen sulfide, and of the ternary mixture were calculated from the following equation, which is derived from basic thermodynamic relationships and the RK1 equation of state:

$$(H - H^*)_0 = \frac{b}{V - b} RT - \frac{a}{T^{1/2}(V + b)} - (3/2) \frac{a}{T^{1/2}} \ln \frac{V + b}{V} \qquad (18)$$

The excess enthalpy, H_n^E, is calculated from

$$H_n^E = H_{m,n} - (X_1 H_{1,n} + X_2 H_{2,n} + X_3 H_{3,n}) \qquad (19)$$

The values for the constants a_i and b_i, and the accentric factors ω_i utilized in these computations, were those reported by Chueh and Prausnitz (*11*, *12*).

It should be remarked that all the coefficients in the equations for the mixture are relative to the pure components, with the only exception for the coefficients k_{ij}, which represent the binary interactions. These coefficients are usually considered as independent of the temperature, pressure, and mole fraction of the components. The interaction coefficients k_{ij} obtained by minimization of the errors for the entire network of the experimental values for the excess enthalpies listed in Table I are presented in Table III.

Equation of State of Redlich-Kwong (RK2). The modifications proposed by Jacoby and Robinson (*10*) to the original Redlich-Kwong equation are as follows:

$$a/R^2 = \alpha + \beta(T - 311) \qquad (20)$$

$$b/R = \gamma + \delta(T - 311) \qquad (21)$$

$$a_{ij} = \tfrac{1}{2}[k_{ij} a_i + (1 - k_{ij}) a_j] \qquad (22)$$

Table III also presents the values of the binary interaction coefficients k_{ij} of eq 22 optimized from the experimental values

Table V. Variation of Binary Iteration Coefficients k_{ij} as Function of Temperature and Pressure

		BWR				RKL				RK2			
T, K	P, MPa	k_{12}	k_{13}	k_{23}	%	k_{12}	k_{13}	k_{23}	%	k_{12}	k_{13}	k_{23}	%
293.15	0.507	0.03	0.28	0.50	6	0.30	0.50	0.50	8	0.70	0.85	−1.60	9
	1.013	0.02	0.20	0.25	7	0.25	0.45	0.05	4	0.60	0.72	−3.00	7
	1.520	0.02	0.20	0.22	4	0.50	0.50	−0.60	3	0.80	0.86	−3.50	6
305.15	0.507	0.013	0.20	0.70	4	0.25	0.50	0.20	6	0.45	0.55	−0.9	15
	1.013	0.013	0.20	0.20	2	0.25	0.40	−0.05	2.5	0.70	0.80	−3.8	4
	1.520	0.010	0.18	0.13	7	0.25	0.35	−0.15	7	0.48	0.66	−2.61	3
313.15	0.507	0.010	0.03	0.550	3	0.11	0.10	0.90	7	0.45	0.30	−1.5	5
	1.013	0.020	0.20	0.068	2	0.11	0.45	0.23	3	0.30	0.65	−3.0	6
	1.520	0.016	0.19	0.080	5	0.10	0.35	0.23	7	0.20	0.60	−2.95	10

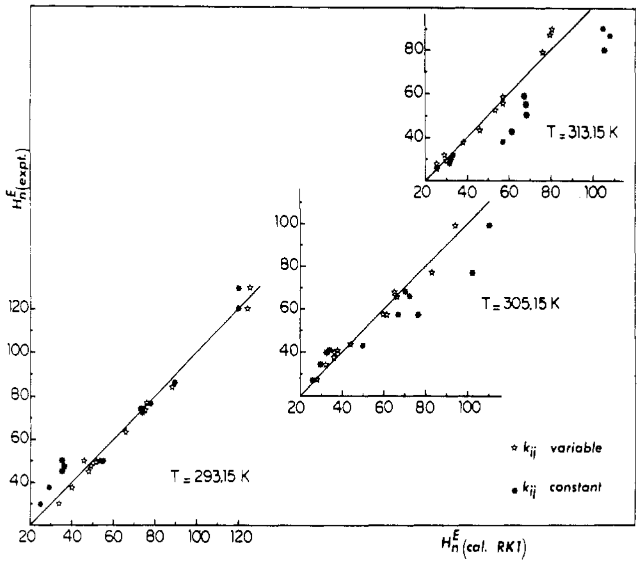

Figure 4. Experimental values of H_n^E vs. values of H_n^E calculated from RK1 equation of state.

for the excess enthalpies listed in Table I.

Equation of State of Benedict-Webb-Rubin (BWR). The equations for the calculation of the enthalpies for the pure components and the ternary mixture and the mixing rules proposed by Bishnoi and Robinson (*13*) are the following:

$$(H - H^*)_n = \left(B_0RT - 2A_0 - \frac{4C_0}{T^2}\right)\rho + (2bRT - 3a)\frac{\rho^2}{2} + \frac{6a\alpha\rho^5}{5} + \frac{c\rho^2}{T^2}\left[\frac{3(1 - e^{-\gamma\rho^2})}{\gamma\rho^2} - \frac{e^{-\gamma\rho^2}}{2} + \gamma\rho^2 e^{-\gamma\rho^2}\right] \quad (23)$$

$$H_n^E = H_{m,n} - (X_1H_{1,n} + X_2H_{2,n} + X_3H_{3,n}) \quad (24)$$

mixing rules

$$A_{0m} = \sum_i\sum_j X_iX_jA_{0ij} \qquad A_{0ij} = (1 - k_{ij})(A_{0i}A_{0j})^{1/2} \quad (25)$$

$$B_{0m} = \sum_i\sum_j X_iX_jB_{0ij} \qquad B_{0ij} = (B_{0i}B_{0j})^{1/2} \quad (26)$$

$$C_{0m} = \sum_i\sum_j X_iX_jC_{0ij} \qquad C_{0ij} = (1 - k_{ij})^3(C_{0i}C_{0j})^{1/2} \quad (27)$$

$$a_m = \sum_i\sum_j\sum_k X_iX_jX_k(a_{ij}a_{jk}a_{ik})^{1/3} \qquad a_{ij} = (1 - k_{ij})(a_ia_j)^{1/2} \quad (28)$$

$$b_m = \sum_i\sum_j\sum_k X_iX_jX_k(b_{ij}b_{jk}b_{ik})^{1/3} \qquad b_{ij} = (b_ib_j)^{1/2} \quad (29)$$

$$c_m = \sum_i\sum_j\sum_k X_iX_jX_k(c_{ij}c_{jk}c_{ik})^{1/3} \qquad c_{ij} = (1 - k_{ij})^3(c_ic_j)^{1/2} \quad (30)$$

$$\alpha_m = \sum_i\sum_j\sum_k X_iX_jX_k(\alpha_{ij}\alpha_{jk}\alpha_{ik})^{1/3} \qquad \alpha_{ij} = (\alpha_i\alpha_j)^{1/2} \quad (31)$$

$$\gamma_m = \sum_i\sum_j X_iX_j\gamma_{ij} \qquad \gamma_{ij} = (\gamma_i\gamma_j)^{1/2} \quad (32)$$

The optimized binary interaction coefficients for the ternary system, as well as those obtained previously for the binary systems methane-carbon dioxide and methane-hydrogen sulfide, are presented, for the three equations of state, in Table III. These binary interaction coefficients, listed in Table III, are independent of temperature and pressure.

The coefficients for the pure components methane, carbon dioxide, and hydrogen sulfide, as well as the equations of state and equations derived for the evaluation of the thermodynamic properties, have been reported in the previous articles (*1*, *2*).

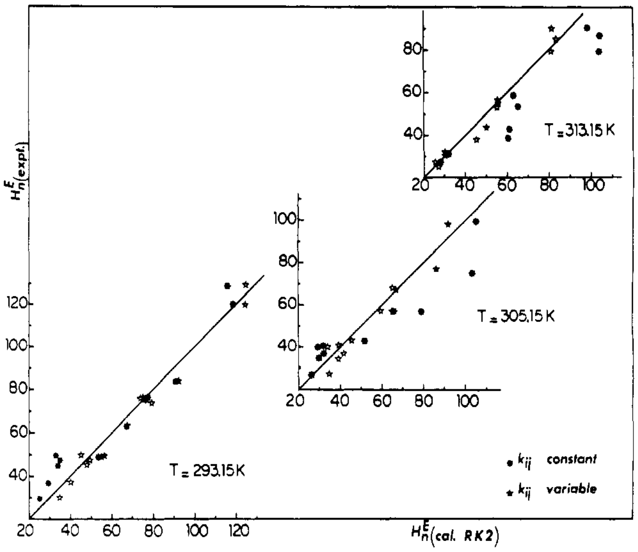

Figure 5. Experimental values of H_n^E vs. values of H_n^E calculated from RK2 equation of state.

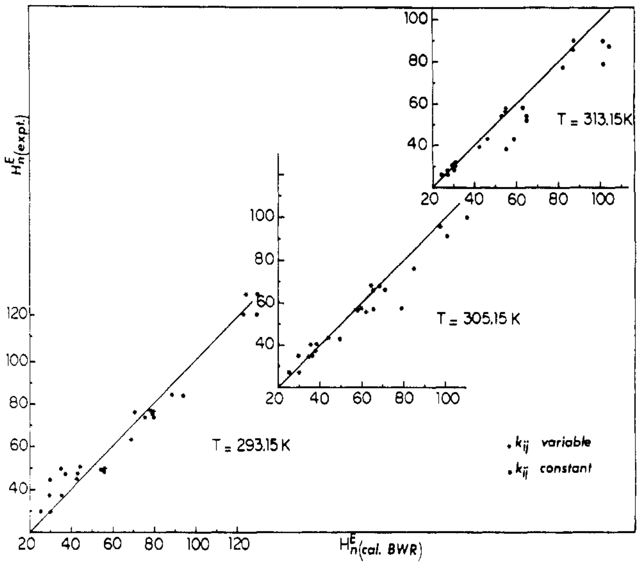

Figure 6. Experimental values of H_n^E vs. values of H_n^E calculated from BWR equation of state.

The comparison between the experimental values of the excess enthalpies and those calculated from the equations of state was performed by utilizing the expression

$$100[(H_{n\,\mathrm{exptl}}^E - H_{n\,\mathrm{calcd}}^E)/H_{n\,\mathrm{exptl}}^E]$$

The mean values for the entire network of experimental results is presented in Table IV. For the three equations of state these values have been obtained by utilizing the values of k_{ij} listed at Table III.

Since the values of the excess enthalpies for the ternary system methane-carbon dioxide-hydrogen sulfide are low, they were replotted in Figures 4-6 in a different manner which portrays in a better way the deviations between experimental and calculated values, which seem to be high at first inspection. However, certain remarks are pertinent, concerning the binary interaction constants k_{12}. Indeed, inspection of Table III reveals that the binary interaction constants k_{12} and k_{13}, previously determined from the experimental results for the binary systems methane-carbon dioxide and methane-hydrogen sulfide, although appreciably different from those for the ternary system, may still be utilized as initial values, in the iterative procedure for the theoretical calculations of the excess enthalpies for the ternary system methane–hydrogen sulfide–carbon dioxide, resulting from combination of these binaries.

Effect of Adjustment of the Binary Iteration Coefficients, k_{ij}, as Function of Temperature and Pressure, on the Predicted Values of Excess Enthalpies

With the purpose of improving the prediction of excess enthalpies, a second series of binary interaction coefficients has been obtained allowing for the possibility of their variation as a function of temperature and pressure. The values of the excess enthalpies calculated from equations of state, which are presented in Table I, were determined by utilizing these adjusted values of the binary interaction coefficients. The values of the excess enthalpies, calculated from the same equations of state, but utilizing values for the binary interaction coefficients independent of temperature and pressure, are presented in ref *14*. In this case, the deviations between experimental and calculated values are considerably higher.

A graphical portrayal of the results in Table I including the theoretical and experimental results is presented in Figures 1–3 as a function of the mole fraction of carbon dioxide in the ternary mixture.

Table V presents the second series of binary interaction coefficients adjusted for temperature and pressure. The column labeled % lists the mean percentage deviations between experimental and calculated values of the excess enthalpies.

The conclusion which can be inferred from inspection of these results is that, as indicated by the column labeled % in Table V, the mean percentage deviation between experimental and calculated values of the excess enthalpies is in most cases below 8%. Consequently, a better prediction of excess enthalpy values can be obtained from the series of binary interaction coefficients, k_{ij}, adjusted as a function of temperature and pressure. Figures 4–6 confirm this fact in an even clearer manner.

The variation of the binary interaction coefficients k_{ij} with temperature and pressure is considerably more pronounced with respect to the coefficient k_{23}, relative to the binary interaction carbon dioxide–hydrogen sulfide. The fact that this system is composed of two polar gases is the probable justification for this behavior.

The question of which of the three equations of state, i.e., RK1, RK2, or BWR, is better suited for the prediction of the excess enthalpy values for the ternary system methane–hydrogen sulfide–carbon dioxide cannot be answered in an indisputable manner. Indeed, inspection of Tables IV and V, comparing experimental and calculated values for the excess enthalpies, reveals relatively low deviations between the mean percentage deviations in all cases. However, when one considers the complexity of the BWR equation, which involves eight individual constants, the choice of the much simpler RK equations becomes very appealing. This conclusion is even more apparent from the results obtained from the utilization of the binary interaction coefficients adjusted as a function of temperature and pressure.

Conclusion

Examination of the values of the excess enthalpies for the three systems H_2S–CO_2, CH_4–CO_2–H_2S, and CH_4–CO_2 reveals that the values for their excess enthalpies decrease in the order just mentioned.

The experimental excess enthalpy data for the ternary system have permitted the determination of two series of binary interaction coefficients k_{ij}. The first series, for which the k_{ij}'s are independent of temperature and pressure, leads to mean percentage deviations between the experimental values of the excess enthalpy and the values calculated from the BWR, RK1, and RK2 equations of state varying from 11% to 21%. The second series, for which the k_{ij}'s are adjusted as a function of temperature and pressure, leads to mean percentage deviations between the experimental values of the excess enthalpy and the values calculated from the BWR, RK1, and RK2 equations of state varying between 2% and 10%. It should be remarked that the coefficient k_{23}, relative to the system carbon dioxide–hydrogen sulfide, varies considerably more as a function of the temperature and pressure than the other two binary interaction coefficients. The fact that the system carbon dioxide–hydrogen sulfide is composed of two polar gases is a probable explanation for this behavior.

It should be also remarked that the coefficients k_{ij} obtained from the treatment of the experimental excess enthalpy data for the binary systems methane–carbon dioxide and methane–hydrogen sulfide may serve as initial values for the iterative procedure leading to the prediction of excess enthalpies of more complex systems, involving these binaries. Indeed, the interaction coefficients for the ternary system were only slightly higher than those for the case of the binary systems.

Glossary

a	coefficient in Redlich–Kwong equation, MPa $K^{1/2}$ cm^6/mol^2
a_{11}, a_{22}, a_{33}, a_{12}, a_{13}, a_{23}	coefficients in Redlich–Kwong equation, defined by eq 11
b	coefficient in Redlich–Kwong equation, cm^3/mol
b_1, b_2	coefficients in Redlich–Kwong equation, defined by eq 17
a, b, c, A_0, B_0, C_0	coefficients in BWR equation of state
C_P	molar heat capacity at constant pressure, J/(mol K)
E_k	kinetic energy, J/mol
F	flow rate, mol/s
H	molar enthalpy, J/mol
k_{12}, k_{13}, k_{23}	binary interaction coefficients, dimensionless
P	pressure, MPa
P_{c12}, P_{c13}, P_{c23}	pseudocritical pressures, defined by eq 13, MPa
Q	energy supplied to gas system by the power supply, J/s
R	universal gas constant, J/(mol K)
T	temperature, K
T_{c12}, T_{c13}, T_{c23}	pseudocritical temperatures, defined by eq 12, K
V	molar volume, cm^3/mol
X	mole fraction, dimensionless
Z_{c12}, Z_{c13}, Z_{c23}	pseudocritical compressibility coefficients, defined by eq 14, dimensionless

Superscripts

E	denotes an excess thermodynamic property
–	denotes mean values for thermodynamic properties (for Joule–Thomson isothermal coefficients, ϕ, and molar heat capacities at constant pressure, C_P)
*	denotes ideal-gas state at a temperature T and pressure $P = 0$

Subscripts

A	denotes pure gas A (CH_4)
B	denotes pure gas B (CO_2)
C	denotes pure gas C (H_2S)
A–C	denotes gas mixture A–C ($CH_4 + H_2S$)
A–B–C	denotes gas mixture A–B–C ($CH_4 + CO_2 + H_2S$)
i	denotes component *i*
m	denotes mixture
n	denotes a nominal outlet condition
1	denotes inlet conditions (P_1, T_1) for gas mixture A–C ($CH_4 + H_2S$)
2	denotes inlet conditions (P_2, T_2) for gas B (CO_2)
0	denotes outlet conditions (P_0, T_0) for the ternary mixture ($CH_4 + H_2S + CO_2$)

Greek Letters

α	constant in BWR equation of state, dm^9/mol^3
γ	constant in BWR equation of state, dm^6/mol^2
α, β, γ, δ	constants in RK2 equation of state, eq 20 and 21; values and units are presented in ref *1*
ΔE_k	change of kinetic energy for gaseous system across calorimeter, J/mol
ΔH	change of molar enthalpy, J/mol
ΔH_m	heat of mixing, J/mol
ρ	gas density, mol/cm^3
ϕ	isothermal Joule–Thomson coefficient, J/(mol MPa)
Ω_a, Ω_b	constants in RK1 equation of state, dimensionless
ω_1, ω_2, ω_3	accentric factors for pure components CH_2, CO_2, and H_2S, respectively, dimensionless

Registry No. CH_4, 74-82-8; CO_2, 124-38-9; H_2S, 7783-06-4.

Literature Cited

(1) Barry, A. O.; Kaliaguine, S. C.; Ramalho, R. S. *J. Chem. Eng. Data* **1982**, *27*, 258–64.
(2) Barry, A. O.; Kaliaguine, S. C.; Ramalho, R. S. *J. Chem. Eng. Data* **1982**, *27*, 436–9.
(3) Ba, L. B.; Nain, V. P. S.; Kaliaguine, S. C.; Ramalho, R. S. *J. Chem. Eng. Data* **1977**, *22*, 171–7.
(4) Ba, L. B.; Kaliaguine, S. C.; Ramalho, R. S. *J. Chem. Thermodyn.* **1978**, *10*, 603–12.
(5) Ba, L. B.; Kaliaguine, S. C.; Ramalho, R. S. *Can. J. Chem. Eng.* **1979**, *57*, 363–6.
(6) Benedict, M.; Webb, G. B.; Rubin, L. C. *J. Chem. Phys.* **1940**, *8*, 334–45.
(7) Tester, H. E. "Thermodynamic Function of Gases"; Butterworths: London, 1961; Vol. 3, pp 1–68.
(8) Lee, B. I.; Kesler, M. G. *AIChE J.* **1975**, *21*, 511–27.
(9) Redlich, O.; Kwong, J. N. S. *Chem. Rev.* **1949**, *44*, 233–40.
(10) Robinson, R. L.; Jacoby, R. H. *Hydrocarbon Process.* **1965**, *44*, 141–5.
(11) Chueh, P. L.; Prausnitz, J. M. *Ind. Eng. Chem. Fundam.* **1967**, *6*, 492–8.
(12) Chueh, P. L.; Prausnitz, J. M. *AIChE J.* **1967**, *13*, *6*, 1099–106.
(13) Bishnoi, P. R.; Robinson, D. B. *Can. J. Chem. Eng.* **1972**, *50*, 2, 101–7.
(14) Barry, A. O. Ph.D. Thesis, Laval University, Quebec, QC, Canada, 1983.

Received for review September 15, 1982. Accepted May 5, 1983.

Densities and Viscosities of Binary Solvent Mixtures of *N*-Methylacetamide with Aliphatic Alcohols

Liisa Pikkarainen

Department of Chemistry, University of Oulu, SF-90570 Oulu 57, Finland

Densities and viscosities of binary liquid mixtures of *N*-methylacetamide (NMA) with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-methyl-2-propanol have been determined at 303.15 K. The excess volume, the excess viscosity, and the excess Gibbs energy of activation of flow have been calculated from the experimental data. The role of intermolecular interactions in the mixtures is discussed, and a comparison made with the corresponding binary mixtures of *N*,*N*-dimethylacetamide (DMA).

Introduction

Comparison of the dielectric properties of N-mono- and N,N-disubstituted amides of carboxylic acids on one hand and those of the amides of sulfonic acids on the other has revealed some interesting features. The dielectric permittivities of N-monosubstituted carboxamides are high and are significantly higher than those of the N,N-disubstituted analogues (*1*–*3*). At the same time, both N-mono- and N,N-disubstituted sulfonamides are characterized by high dielectric permittivities, with somewhat greater values for the N-monosubstituted amides (*1*). The high permittivities of N-monosubstituted carboxamides have been ascribed to formation of long N—H···O═C hydrogen-bonded chains (*3*, *4*), whose existence is supported by spectroscopic studies (*5*, *6*). N-Monosubstituted sulfonamides, for their part, appear to self-associate to cyclic polymers (*7*, *8*), and the high permittivities have been related mainly to the large dipole moments (*1*).

Our recent studies have dealt with the properties of binary mixtures of aliphatic alcohols with *N*-methyl- and *N*,*N*-dimethylmethanesulfonamide (*9*, *10*) and with *N*,*N*-dimethylacetamide (DMA) (*11*). To explore more fully the findings outlined above we continue now with studies on the mixtures of *N*-methylacetamide. Here we report the densities and viscosities of binary mixtures of *N*-methylacetamide (NMA) with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-methyl-2-propanol at 303.15 K.

Experimental Section

Materials. Alcohols were the same as in the previous studies (*9*–*11*). *N*-Methylacetamide (a purum product of Fluka AG, Switzerland) was purified by distillation under reduced pressure followed by fractional crystallizations (*12*).

Measurements were carried out with a digital density meter DMA 40 (Anton Paar K.G., Austria) and Cannon-Ubbelohde viscometers (Cannon Instrument Co, USA) (*13*) as before (*9*–*11*). The viscosities are expressed in units of centipoise equal to 10^{-3} N s m^{-2}. The experimental values of the density and viscosity of *N*-methylacetamide were 0.950 28 g cm^{-3} and 3.829 cP at 303.15 K (literature values 0.9503 g cm^{-3} (*14*) and 3.836 cP (*15*) (an interpolated value), respectively).