

## Conclusion

Accurate low-pressure VLE of isobutyraldehyde/ethyl acetate/DMF and the constituent binaries have been obtained. The lowering of the relative volatility of isobutyraldehyde/ethyl acetate by DMF in their ternary mixture can be understood in terms of the chemical interaction between DMF and the aldehyde group. All models considered, except the van Laar model, predict the behavior of the isobutyraldehyde/ethyl acetate/DMF ternary mixture accurately with only binary information. The DMF-aldehyde group interaction in the isobutyraldehyde/DMF and DMF/benzaldehyde mixtures are significantly different as discussed above, and the UNIFAC group contribution model cannot describe both mixtures accurately with one set of DMF-aldehyde parameters.

## Acknowledgment

We thank Huey Wu for his assistance in the calculations reported here.

**Registry No.** DMF, 68-12-2; isobutyraldehyde, 78-84-2; ethyl acetate, 141-78-6.

## Literature Cited

- (1) Kassmann, K.; Knapp, H. *Ber. Bunsenges. Phys. Chem.*, in press.
- (2) Eng, R.; Sandler, S. I. *J. Chem. Eng. Data* **1984**, *29*, 156.
- (3) Shealy, G. S.; Sandler, S. I. *J. Chem. Thermodyn.* **1985**, *17*, 143.
- (4) Shealy, G. S.; Sandler, S. I. *J. Chem. Eng. Data* **1985**, *30*, 455.
- (5) Fredenslung, A.; Gmehling, J.; Rasmussen, P. *Vapor-Liquid Equilibrium Using UNIFAC*; Elsevier: Amsterdam, 1977.
- (6) Hayden, J. G.; O'Connell, J. P. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209.
- (7) Holmes, M. J.; van Winkle, M. *Ind. Eng. Chem.* **1970**, *62*, 21.

Received for review December 23, 1985. Revised May 12, 1986. Accepted June 16, 1986. We acknowledge the support of the National Science Foundation (Grant No. CPE 8316913) to the University of Delaware and of the Deutsche Forschungsgemeinschaft to the Technical University of Berlin. In addition, Torsten Hauschild wishes to express his gratitude to the Ernest Solvay Stiftung for a research scholarship for study in the United States.

# Thermodynamic Properties of Dichloromethane Gas

Rakesh P. Singh

Department of Chemical Engineering, Indian Institute of Technology, Kanpur 208 016, India

**Virial coefficients, derived from an analysis of precise  $P-V-T$  data, form a basis for the determination of thermodynamic properties and the force constants of appropriate intermolecular potential models. An earlier work reports experimental  $P-V-T$  measurements for dichloromethane gas from about 350 to 510 K along with compression factors and second virial coefficients. This study presents revised values of second virial coefficients and the following other derived quantities (the figure in parentheses indicates the estimated percent uncertainty): (I) third virial coefficients (2-20); (II) Stockmayer (12-6-3) force constants; (III) thermodynamic properties (0.2-0.5 up to 10 atm, increasing to 5 at 30 atm and above); and (IV) fugacity coefficients. Stockmayer force constants of this work, evaluated from the revised second virial coefficients, are in close agreement with literature values. The experimental third virial coefficients are reported for the first time here. Though the uncertainty in these values is large, the usefulness of the values is considerable as is evident from the excellent agreement of the present entropy values with those available in the literature.**

## Introduction

The present investigation is a part of an extensive research program for evaluating the chemical thermodynamic properties of selected halogenated alkanes over a wide range of temperatures and pressures. The volumetric properties of dichloromethane gas from about 350 to 510 K at pressures below the saturation pressure at each temperature were determined by using a Kay-type apparatus which was fabricated in

a previous investigation (1). The compression factors and second virial coefficients computed from the measured  $P, V, T$  values, with the estimated percent uncertainties of 0.02-0.5 and 0.5, respectively, have been reported elsewhere (1).

Virial coefficients, derived from an analysis of precise  $P-V-T$  data, form a basis for the determination of thermodynamic properties and the force constants of suitable potential models. No experimental values are available for the third and higher virial coefficients of dichloromethane. Using the second virial coefficient data of Perez Masia and Diaz Pena (2) in the range 349.53-510.0 K and those of Fogg et al. (3) in the range 319.4-382.6 K as compiled by Dymond and Smith (4), Polak and Lu (5) evaluated the parameters of the Stockmayer (12-6-3) potential function. Rätzsch and Freydank (6) report the parameters of the Stockmayer (18-6-3) potential. Dzung (7) calculated the thermodynamic properties of dichloromethane up to a temperature of 423 K and a pressure of about 2.6 atm, using published values of the specific heat capacity of the saturated liquid and other pertinent data. Seshadri et al. (8) extended the range of Dzung's work by computing the thermodynamic properties of dichloromethane up to a temperature of 750 K and a pressure of 200 atm by using the 11-constant Martin-Hou equation of state (9).

This work reports revised values of second virial coefficients and the following other quantities derived from the experimental  $P-V-T$  data (1) (the figure in parentheses indicates the estimated percent uncertainty): (i) third virial coefficients (2-20); (ii) Stockmayer (12-6-3) force constants; (iii) thermodynamic properties (0.2-0.5 up to 10 atm, increasing to 5 at 30 atm and above); and (iv) fugacity coefficients. The experimental third virial coefficients are reported for the first time in the present investigation. The revised second virial coefficients are of a higher precision than those reported earlier (1), these values and the present third virial coefficients being very nearly consistent with each other.

## Theoretical Background

**1. The Virial Equation of State.** The virial equation of state expresses the deviations from ideality as an infinite power series in the density,  $1/V$  (Leiden series)

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \dots \quad (1)$$

or, in the pressure,  $P$  (Berlin series)

$$Z = \frac{PV}{RT} = 1 + B'P + C'P^2 + \dots \quad (2)$$

The coefficients of the two expansions are uniquely interrelated as follows (10):

$$B' = B/RT; \quad B = B'RT \quad (3)$$

$$C' = (C - B^2)/(RT)^2; \quad C = (C' + B'^2)(RT)^2 \quad (4)$$

**2. Thermodynamic Properties.** The thermodynamic properties of a real gas are commonly expressed in the form of departure functions. For example,  $[H(T) - H^\circ(T)]$  is the enthalpy of the gas in the real state less that of the gas in the standard state (ideal gas at 1 atm) at the same temperature. Departure functions are related to the second and third virial coefficients as follows:

$$[U(T) - U^\circ(T)] = -RT \left[ \frac{T}{V} \frac{dB}{dT} + \frac{T}{2V^2} \frac{dC}{dT} \right] \quad (5)$$

$$[H(T) - H^\circ(T)] = RT \left[ \frac{1}{V} \left( B - T \frac{dB}{dT} \right) + \frac{1}{V^2} \left( C - \frac{T}{2} \frac{dC}{dT} \right) \right] \quad (6)$$

$$[S(T) - S^\circ(T)] = -R \left[ \ln P + \frac{T}{V} \frac{dB}{dT} + \frac{B^2}{2V^2} - \frac{C}{2V^2} + \frac{T}{2V^2} \frac{dC}{dT} \right] \quad (7)$$

$$[G(T) - G^\circ(T)] = RT(B'P + C'(P^2/2)) + RT \ln P \quad (8)$$

**3. Fugacity Coefficient.** The fugacity coefficient,  $\varphi$ , is related to  $B'$  and  $C'$  as

$$\ln \varphi = B'P + C'(P^2/2) \quad (9)$$

## Results and Discussion

**1. Virial Coefficients.** The quantities,  $B_v$  and  $C_v$ , defined by eq 10 and 11, were calculated from the isothermal  $P$ - $V$ - $T$

$$B_v = (Z - 1)V; \quad B = \lim_{(1/V) \rightarrow 0} B_v \quad (10)$$

$$C_v = [(Z - 1)V - B]V; \quad C = \lim_{(1/V) \rightarrow 0} C_v \quad (11)$$

data reported in an earlier work (1) and extrapolated to zero density to obtain  $B$  and  $C$  given in Table I. The shapes of the  $C_v$  curves are so sensitive to the value chosen for  $B$  that they provide excellent criteria for extrapolating the  $B_v$  curves to zero density (11). A small deviation from the "correct" values of

**Table I. Second and Third Virial Coefficients for Dichloromethane**

$T/K$	$B/(\text{cm}^3 \text{ mol}^{-1})$	$C \times 10^{-6}/(\text{cm}^6 \text{ mol}^{-2})$
349.53	-546.9	
368.07	-476.8	0.29
389.71	-413.8	0.27
411.65	-365.4	0.26
431.68	-322.9	0.24
451.71	-292.0	0.23
471.86	-262.5	0.20
492.25	-239.7	0.18
502.44	-227.1	0.17
510.00	-220.9	

$B$  results in unreasonably large positive or negative curvature in the plots of  $C_v$  at low densities. Thus, the values of  $B$  were selected so that the  $C_v$  plots had a small, nearly constant curvature at low densities. Not only are the extrapolated values for  $B$  and  $C$  very nearly consistent with each other, but more precise values can be assigned to  $B$  than previously reported (1), e.g., in the order of  $\pm 0.15 \text{ cm}^3 \text{ mol}^{-1}$  at 492.25 K in comparison to  $\pm 1.4 \text{ cm}^3 \text{ mol}^{-1}$  (1). The uncertainty in  $C$  values is estimated to be about 20% at 368.07 K and decreases to about 2% at 471.86 K and above (up to near  $T_c$ ). The  $C$  values at the two extreme temperatures, 349.53 and 510 K ( $T_c$ ), had much larger uncertainty as compared to those at intermediate temperatures and hence are not reported. The present  $C$  values are the only ones available so far.

Computation of  $Z$  using  $B$  values only is recommended up to about 1.5 atm at each temperature. Inclusion of  $C$  values results in the prediction of  $Z$  to within 0.5% of the experimental compression factors at high pressures. However, at the highest pressures additional correction is necessary implying the necessity of at least the fourth virial coefficient,  $D$ . Because of a large scatter in  $\{[(Z - 1)V - B]V - C\}V$  vs.  $1/V$  plots at most of the isotherms, it was not possible to get reasonable estimates for  $D$ .

For ease of interpolation and limited extrapolation and for calculating gas-phase nonideality, the  $B$  and  $C$  values given in Table I were fitted to a polynomial in  $1/T$ .

$$B = 207.72 - 289.35 \times 10^3 T^{-1} + 961.54 \times 10^5 T^{-2} - 304.1 \times 10^8 T^{-3} \quad (12)$$

$$C = -95.6 \times 10^3 + 87.1 \times 10^8 T^{-1} - 15.2 \times 10^9 T^{-2} \quad (13)$$

The standard deviations of the fit for  $B$  and  $C$  were  $1.48 \text{ cm}^3 \text{ mol}^{-1}$  and  $0.043 \times 10^4 \text{ cm}^6 \text{ mol}^{-2}$ , respectively.

**2. Thermodynamic Properties and Fugacity Coefficients.** Thermodynamic properties  $[U(T) - U^\circ(T)]$ ,  $[H(T) - H^\circ(T)]$ , and  $[S(T) - S^\circ(T)]$  were calculated at the experimental  $P, V$  values for a particular isotherm from eq 5, 6, and 7, respectively. In evaluating  $[G(T) - G^\circ(T)]$  from eq 8,  $B'$  and  $C'$  were obtained from eq 3 and 4, respectively. In a similar manner, the fugacity coefficients,  $\varphi$ , were calculated from eq 9. Appropriate derivatives of the virial coefficients were obtained from eq 12 and 13. The computed thermodynamic properties and fugacity coefficients are reported in Table II. The error in the derived thermodynamic properties is estimated to be 0.2–0.5% up to a pressure of about 10 atm, increasing to 5% at 30 atm and above.

The agreement of the present entropy values with those of Seshadri et al. (8) is excellent as shown in Table III. Ideal gas entropy values,  $S^\circ$ , were taken from ref 12. Comparison of the  $H$  values was not possible because of the difference in the choice of standard states.

Table II. Thermodynamic Properties and Fugacity Coefficients for Dichloromethane<sup>a</sup>

$T/K$	$P/\text{atm}$	$-[U(T) - U^\circ(T)]/$ (cal mol <sup>-1</sup> )	$-[H(T) - H^\circ(T)]/$ (cal mol <sup>-1</sup> )	$[G(T) - G^\circ(T)]/$ (cal mol <sup>-1</sup> )	$[S(T) - S^\circ(T)]/$ (cal mol <sup>-1</sup> K <sup>-1</sup> )	$\phi$	
349.53	0.14922	5.04	7.01	-1323.3	3.7659	0.9972	
	0.22311	7.54	10.5	-1044.9	2.9594	0.9958	
	0.26727	9.04	12.6	-920.0	2.5962	0.9949	
	0.46091	15.7	21.8	-544.1	1.4943	0.9912	
	0.85752	29.4	40.8	-118.2	0.2212	0.9837	
	2.4088	85.2	118.4	578.2	-1.9927	0.9543	
	2.4283	85.9	119.4	583.5	-2.0108	0.9540	
368.07	0.14852	4.31	6.04	-1396.6	3.7779	0.9976	
	0.17485	5.08	7.11	-1277.5	3.4515	0.9972	
	0.26232	7.63	10.7	-981.8	2.6385	0.9958	
	0.45257	13.2	18.5	-585.1	1.5396	0.9928	
	0.86531	25.5	35.7	-115.9	0.2182	0.9863	
	2.3390	70.4	98.5	594.0	-1.8812	0.9630	
	2.7806	84.4	117.9	715.2	-2.2633	0.9561	
	3.5368	108.8	152.0	882.0	-2.8090	0.9442	
	4.1191	128.1	179.0	986.3	-3.1655	0.9351	
	389.71	0.14781	3.65	5.14	-1482.1	3.7898	0.9981
0.18433		4.55	6.41	-1311.4	3.3487	0.9976	
0.25397		6.28	8.84	-1063.9	2.7074	0.9967	
0.42128		10.4	14.7	-673.7	1.6910	0.9945	
0.83148		20.7	29.2	-151.3	0.3135	0.9892	
2.4457		62.2	87.6	667.7	-1.9378	0.9683	
2.9259		75.0	105.4	801.5	-2.3271	0.9621	
3.5766		92.6	130.1	950.3	-2.7718	0.9537	
4.3025		112.5	158.0	1085.7	-3.1912	0.9444	
7.4752		205.6	288.3	1479.6	-4.5349	0.9039	
411.65		0.14282	3.03	4.29	-1593.3	3.8600	0.9985
		0.17594	3.74	5.29	-1423.0	3.4439	0.9981
		0.22265	4.73	6.70	-1230.8	2.9736	0.9976
	0.33816	7.20	10.2	-889.9	2.1371	0.9964	
	0.81545	17.4	24.7	-174.1	0.3630	0.9912	
	2.4459	53.3	75.3	709.9	-1.9073	0.9737	
	2.6428	57.7	81.5	771.4	-2.0720	0.9716	
	2.9533	64.7	91.4	859.5	-2.3098	0.9683	
	3.4014	74.9	105.8	971.0	-2.6157	0.9635	
	4.0173	89.0	125.8	1101.6	-2.9813	0.9569	
	4.5860	102.3	144.5	1204.7	-3.2772	0.9509	
	7.3457	169.6	239.1	1564.5	-4.3807	0.9216	
	11.681	287.0	403.5	1902.6	-5.5987	0.8762	
	431.68	0.15742	2.95	4.19	-1587.2	3.6672	0.9986
		0.21008	3.94	5.59	-1340.1	3.0914	0.9981
0.25848		4.85	6.88	-1162.6	2.6773	0.9976	
0.37229		6.99	9.92	-850.5	1.9473	0.9966	
0.72729		13.7	19.4	-278.9	0.6010	0.9933	
1.0390		19.6	27.8	24.6	-0.1215	0.9905	
2.4231		46.3	65.7	740.0	-1.8664	0.9779	
2.6383		50.5	71.6	811.3	-2.0453	0.9759	
2.8946		55.5	78.8	888.8	-2.2413	0.9736	
3.2174		61.9	87.8	976.9	-2.4663	0.9706	
3.5886		69.3	98.2	1067.5	-2.7005	0.9672	
3.9484		76.5	108.4	1146.6	-2.9073	0.9640	
4.2901		83.4	118.2	1215.0	-3.0884	0.9609	
11.595		243.2	343.4	2007.3	-5.4441	0.8953	
451.71		0.15298	2.55	3.63	-1686.3	3.7252	0.9988
		0.17506	2.92	4.16	-1565.5	3.4565	0.9986
		0.21838	3.64	5.19	-1367.3	3.0155	0.9983
		0.26678	4.45	6.34	-1188.0	2.6159	0.9979
	0.41286	6.90	9.82	-797.0	1.7427	0.9968	
	0.81627	13.7	19.5	-188.0	0.3731	0.9936	
	2.3262	39.4	56.1	741.3	-1.7651	0.9817	
	2.5060	42.5	60.5	806.8	-1.9200	0.9803	
	2.7153	46.1	65.6	877.3	-2.0875	0.9787	
	2.9475	50.2	71.3	949.3	-2.2595	0.9769	
	3.1378	53.5	76.1	1004.1	-2.3913	0.9754	
	3.3631	57.4	81.6	1064.7	-2.5378	0.9736	
	3.7410	64.0	91.1	1157.6	-2.7643	0.9707	
	4.1368	71.0	101.0	1246.0	-2.9798	0.9676	
	4.6090	79.4	112.9	1338.6	-3.2134	0.9639	
	26.485	579.9	814.5	2739.9	-7.8534	0.7991	
	471.86	0.14605	2.19	3.12	-1804.8	3.8183	0.9990
		0.18682	2.80	3.99	-1574.2	3.3278	0.9987
		0.21994	3.30	4.70	-1421.4	3.0024	0.9985
0.26920		4.03	5.75	-1232.2	2.5992	0.9982	
0.37112		5.56	7.93	-931.8	1.9580	0.9975	
0.59788		8.98	12.8	-486.1	1.0031	0.9959	
0.98174		14.8	21.1	-23.5	0.0053	0.9933	

Table II (Continued)

$T/K$	$P/\text{atm}$	$-[U(T) - U^\circ(T)]/$ (cal mol <sup>-1</sup> )	$-[H(T) - H^\circ(T)]/$ (cal mol <sup>-1</sup> )	$[G(T) - G^\circ(T)]/$ (cal mol <sup>-1</sup> )	$[S(T) - S^\circ(T)]/$ (cal mol <sup>-1</sup> K <sup>-1</sup> )	$\phi$	
492.25	2.5127	38.2	54.4	847.8	-1.9120	0.9830	
	2.8422	43.3	61.7	961.2	-2.1678	0.9807	
	3.2594	49.7	70.8	1087.0	-2.4537	0.9779	
	3.7977	58.1	82.8	1226.8	-2.7754	0.9743	
	4.5293	69.6	99.1	1387.3	-3.1501	0.9694	
	5.7655	89.4	127.2	1606.1	-3.6734	0.9610	
	7.3117	114.5	162.8	1818.1	-4.1980	0.9507	
	28.219	528.8	745.3	2939.9	-7.8014	0.8149	
	32.577	645.8	907.5	3042.8	-8.3571	0.7877	
	0.12885	1.75	2.49	-2005.2	4.0684	0.9992	
	0.16452	2.23	3.18	-1766.3	3.5818	0.9990	
	0.20614	2.79	3.98	-1546.0	3.1325	0.9988	
	0.27663	3.75	5.35	-1258.6	2.5461	0.9984	
	0.37345	5.06	7.22	-965.6	1.9470	0.9978	
	0.53822	7.31	10.4	-609.1	1.2162	0.9968	
	1.0257	14.0	19.9	18.9	-0.0788	0.9940	
	2.4641	33.8	48.1	867.9	-1.8608	0.9855	
	2.7537	37.8	53.9	974.9	-2.0899	0.9838	
	3.0294	41.6	59.3	1066.6	-2.2873	0.9822	
	3.4463	47.5	67.6	1190.3	-2.5554	0.9797	
	3.9481	54.5	77.7	1320.3	-2.8400	0.9768	
	4.5258	62.7	89.3	1450.5	-3.1281	0.9734	
	5.5292	77.0	109.6	1640.5	-3.5553	0.9676	
	31.280	517.9	731.3	3176.2	-7.9314	0.8220	
	35.351	608.7	857.9	3269.3	-8.3742	0.8000	
	502.44	0.11231	1.45	2.07	-2183.7	4.3421	0.9994
		0.14883	1.92	2.74	-1902.8	3.7817	0.9992
		0.19299	2.49	3.56	-1643.6	3.2642	0.9989
		0.24565	3.17	4.53	-1403.0	2.7834	0.9986
		0.33907	4.39	6.25	-1081.7	2.1405	0.9981
		0.48430	6.27	8.94	-726.6	1.4283	0.9973
		0.99810	12.9	18.5	-7.40	-0.0220	0.9945
2.4476		32.0	45.5	880.2	-1.8425	0.9866	
2.7645		36.1	51.5	1000.0	-2.0928	0.9848	
3.2276		42.3	60.3	1152.1	-2.4129	0.9823	
3.7798		49.6	70.7	1306.7	-2.7414	0.9793	
4.3471		57.2	81.5	1443.1	-3.0345	0.9762	
4.9637		65.6	93.4	1572.1	-3.3148	0.9728	
5.6894		75.4	107.4	1704.3	-3.6057	0.9688	
32.547		505.0	713.8	3287.7	-7.9595	0.8271	
37.401		603.6	851.5	3396.4	-8.4476	0.8025	
47.023		837.1	1175.3	3563.9	-9.4182	0.7549	
510.00		0.12122	1.51	2.16	-2139.2	4.1903	0.9994
		0.16283	2.04	2.90	-1840.4	3.6029	0.9991
		0.21889	2.74	3.90	-1540.8	3.0135	0.9989
	0.28768	3.60	5.13	-1264.2	2.4688	0.9985	
	0.44904	5.62	8.01	-813.8	1.5800	0.9976	
	0.66814	8.37	11.9	-412.2	0.7849	0.9965	
	1.0613	13.3	19.0	54.7	-0.1444	0.9944	

<sup>a</sup> Note: More significant figures are given to retain internal consistency.

Table III. Comparison of Real Gas Entropy Values for Dichloromethane at 431.68 and 502.44 K

$T/K$	$P/\text{atm}$	$S/(\text{cal mol}^{-1} \text{K}^{-1})$	
		this work	Seshadri et al. (8) <sup>a</sup>
431.68	0.20		72.814
	0.21	72.624	
	1.00		69.570
	1.04	69.412	
	2.89	67.293	
	3.00		67.275
	10.0		64.430
	11.6	64.089	
502.44	0.10		76.527
	0.11	76.225	
	0.19	75.147	
	0.20		75.147
	0.48	73.311	
	0.50		73.317
	1.00	71.861	71.927
	4.96	68.568	
	5.00		68.609
	30.0		64.043
	32.5	63.923	
	47.0	62.465	
50.0		61.402	

<sup>a</sup> Values interpolated in temperatures.

**3. Force Constants for the Stockmayer (12-6-3) Potential (13).** Parameters of the Stockmayer (12-6-3) potential,  $\epsilon/k$  and  $\sigma$ , given in Table IV were evaluated from the  $B$  values by the trial and error procedure described in detail by Hirschfelder et al. (14). The values of  $k$  and  $N_A$  used were those given by Cohen and Taylor (15), and the dipole moment was taken from McClellan (16). Table IV also compares the present values with those evaluated by Polak and Lu (5) by a least-squares regression analysis, and with the values of the Stockmayer (18-6-3) potential parameters given by Rätzsch and Freydanck (6). The agreement between the present values of  $\epsilon/k$  and those of Polak and Lu based on the  $B$  data of Perez Masia and Diaz Pena (2) is excellent, whereas our  $b_0$ ,  $t^*$ , and  $\sigma$  values are closer to those of Polak and Lu based on the  $B$  data of Fogg et al. (3). This discrepancy may be due to, in part, the difference in the technique of evaluation and also the inclusion of  $B$  values at higher temperatures in this work. However, the reliability of the present force constants,  $\epsilon/k$  and  $\sigma$ , was test checked by computing  $B$  values at 431.68 K using the elaborate procedure and newer tables of Gallagher and Klein (17). Agreement between the experimental and the calculated  $B$  was within 0.5%. The present values of  $\epsilon/k$  and  $\sigma$  can therefore be used in computing second virial coefficients from the Stockmayer (12-6-3) potential within reasonable accuracy.

Table IV. Comparison of the Stockmayer Force Constants for Dichloromethane

potential model	<i>N</i>	$\mu/D$	$\sigma/\text{\AA}$	$(\epsilon/k)/\text{K}$	$b_0/(\text{cm}^3 \text{mol}^{-1})$	$t^*$	temp. range/ K	ref
(12-6-3)	7	1.631	2.764	672.6	26.63	0.48	319.4-382.6	5
(12-6-3)	5	1.631	3.150	716.6	39.42	0.304	323.16-423.16	5
(12-6-3)	10	1.631	2.648	715.29	23.423	0.513	349.53-510	this work
(18-6-3)	7	1.631	3.80	642.62			323.16-423.16	6

### Acknowledgment

I acknowledge valuable suggestions provided by Prof. D. R. Douslin on an early version of this paper.

### Glossary

$b_0$	second virial coefficient for a rigid sphere of diameter $\sigma$ , $\text{cm}^3 \text{mol}^{-1}$
$B$	second virial coefficient in eq 1, $\text{cm}^3 \text{mol}^{-1}$
$B'$	second virial coefficient in eq 2, $\text{atm}^{-1}$
$C$	third virial coefficient in eq 1, $\text{cm}^6 \text{mol}^{-2}$
$C'$	third virial coefficient in eq 2, $\text{atm}^{-2}$
$G$	Gibbs energy, $\text{cal mol}^{-1}$
$H$	enthalpy, $\text{cal mol}^{-1}$
$k$	Boltzmann constant, $\text{J K}^{-1}$
$N$	number of experimental points
$N_A$	Avogadro number, $\text{mol}^{-1}$
$P$	pressure, atm
$R$	gas constant, $\text{cm}^3 \text{atm K}^{-1} \text{mol}^{-1}$
$S$	entropy, $\text{cal mol}^{-1} \text{K}^{-1}$
$t^*$	parameter in the Stockmayer potential
$T$	temperature, K
$T_c$	critical temperature, K
$U$	internal energy, $\text{cal mol}^{-1}$
$V$	molar volume, $\text{cm}^3 \text{mol}^{-1}$
$Z$	compression factor
$\epsilon$	parameter in the Stockmayer potential, J
$\mu$	dipole moment, D
$\varphi$	fugacity coefficient
$\sigma$	parameter in the Stockmayer potential, $\text{\AA}$

### Superscript

<sup>o</sup> property of the substance in its standard state

Registry No. Dichloromethane, 75-09-2.

### Literature Cited

- (1) Singh, R. P.; Kudchadker, A. P. *J. Chem. Thermodyn.* **1979**, *11*, 205.
- (2) Perez Masia, A.; Diaz Pena, M. *An. R. Soc. Esp. Fis. Quim. (Madrid)* **1958**, *54B*, 661.
- (3) Fogg, P. G. T.; Hank, P. A.; Lambert, J. D. *Proc. R. Soc. London* **1953**, *A219*, 490.
- (4) Dymond, J. H.; Smith, E. B. *The Virial Coefficients of Gases - A Critical Compilation*; Clarendon: Oxford, U.K., 1969.
- (5) Polak, J.; Lu, B. C.-Y. *Can. J. Chem. Eng.* **1972**, *50*, 553.
- (6) Rätzsch, M. T.; Freydank, H. *Z. Phys. Chem. (Leipzig)* **1973**, *253* (5-6), 393.
- (7) Dzung, L. S. *Brown Boverly Rev.* **1946**, *33*, 158.
- (8) Seshadri, D. N.; Viswanath, D. S.; Kuloor, N. R. *J. Indian Inst. Sci.* **1967**, *49*, 117.
- (9) Martin, J. J.; Hou, Y. C. *AIChE J.* **1955**, *1*, 142.
- (10) Mason, E. A.; Spurling, T. H. *The Virial Equation of State*; Pergamon: Oxford, U.K., 1969.
- (11) Douslin, D. R.; Harrison, R. H.; Moore, R. T.; McCullough, J. P. *J. Chem. Phys.* **1961**, *35*, 1357.
- (12) Rodgers, A. S.; Chao, J.; Wilhoit, R. C.; Zwolinski, B. J. *J. Phys. Chem. Ref. Data* **1974**, *3*, 117.
- (13) Stockmayer, W. H. *J. Chem. Phys.* **1941**, *9*, 398.
- (14) Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. *Molecular Theory of Gases and Liquids*; Wiley: New York, 1954.
- (15) Cohen, E. R.; Taylor, B. N. *J. Phys. Chem. Ref. Data* **1973**, *2*, 663.
- (16) McClellan, A. L. *Tables of Experimental Dipole Moments*; W. H. Freeman: San Francisco, 1963.
- (17) Gallagher, J. S.; Klein, M. J. *Res. Natl. Bur. Stand.* **1971**, *75A*(4), 337.

Received for review August 9, 1985. Revised manuscript received May 5, 1986. Accepted May 27, 1986.

## Ion-Exchange Equilibria: Study of the $\text{Na}^+/\text{Mn}^{2+}$ , $\text{Na}^+/\text{Ni}^{2+}$ , and $\text{Na}^+/\text{Cu}^{2+}$ Exchanges on Several Lewatit Cation Exchangers

Gonzalo Vázquez, Alberto Arce, and Ramón Méndez\*

Departamento de Ingeniería Química, Universidad de Santiago de Compostela, Spain

Rafael Blázquez

Colegio Universitario de La Coruña, Universidad de Santiago de Compostela, Spain

Experimental equilibrium data of several Lewatit +  $\text{Na}^+$  +  $\text{B}^{2+}$  ion-exchange binary systems are given under various conditions: (I) with three exchangers of different cross-linking degree (S-100, S-115, and SP-120); (II) with two sizes of particles (SP-120:  $D_1 = 0.74 \text{ mm}$ , and  $D_2 = 0.96 \text{ mm}$ ); (III) at three total ionic concentration levels of the solution phase (1, 0.1, and 0.01 N); and (IV) with three different counterions ( $\text{B}^{2+} = \text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cu}^{2+}$ ). By means of a previously developed method, where the Wilson equation is employed to evaluate the activity coefficients in the resin phase, the equilibrium constants are determined. The influence of the above variables is studied by using these equilibrium constants.

### Introduction

The variables that can influence the equilibrium in a ion-exchange system can be classified in three groups: (1) those that depend on the exchanger such as the type of exchanger, cross-linking degree, and size of the particle; (2) variables that depend on the solution phase such as the kind of solvent, the set of ions involved, both interchangeable and uninterchangeable, and the total ionic concentration; and (3) those that depend on the working conditions such as pressure or temperature.

In order to carry out a systematic study of ion-exchange equilibrium it seems necessary to establish previously a parameter or a set of parameters that characterize in the best possible way such equilibrium. In a previous paper (1), the