Table V. Plait Points

Salt	Coolidge			Othmer and Tobias			Rectilinear Diameters		
	X_1	X_2	X_3	X_1	X_2	X_3	X_1	X_2	X_3
$KC_2H_3O_2$	0.515	0.022	0.463	0.501	0.024	0.475	0.504	0.025	0.471
$LiC_2H_3O_2$	0.492	0.020	0.488	0.483	0.018	0.499	0.490	0.020	0.490
LiCl	0.480	0.020	0.500	0.488	0.019	0.493	0.473	0.018	0.509
Li_2SO_4	0.435	0.017	0.548	0.427	0.017	0.556	0.434	0.017	0.549

The authors conclude that the tie lines for the present systems are most conveniently correlated by the conjugate curve of Coolidge, or of Sherwood, with the plait point estimated by rectilinear diameters.

LITERATURE CITED

(1) Bachman, I., *Ind. Eng. Chem., Anal. Ed.* **12,** 38 (1940).
(2) Brancker, A. V., Hunter, T. G., Nash, A. W., *Ibid.*, **12,** 35 (1940).
(3) Cailletet, L., Mathias, *Compt. Rend.* **102,** 1202 (1886).
(4) Coolidge, A. S., "International Critical Tables," Vol. III, pp. 398–403, McGraw-Hill, New York, 1928.
(5) Hand, D. B., *J. Phys. Chem.* **34,** 1961 (1930).
(6) Nernst, W., *Z. Physik. Chem.* **8,** 110 (1891).
(7) Othmer, D. F., Tobias, P. E., *Ind. Eng. Chem.* **34,** 693 (1942).
(8) Renard, J. A., J. Chem. Eng. Data **11,** 169 (1966).
(9) Renard, J. A., Oberg, A. G., *Ibid.*, **10,** 152 (1965).
(10) Sherwood, T. K., Pigford, R. L., "Absorption and Extraction," 2nd ed., p. 402, McGraw-Hill, New York, 1952.
(11) Sohio Chemical Co., "Technical Information Bulletin," p. 37, 1960.
(12) Weber, H. C., Meissner, H. P., "Thermodynamics for Chemical Engineers," p. 466, Wiley, New York, 1957.

Received for review July 25, 1966; Accepted October 20, 1966. Part of a work performed under a grant appropriated by the State of Texas.

Volume Changes of Mixing: Dichloromethane with Acetone and Methyl Acetate

H. C. VAN NESS and R. L. MACHADO[1]
Chemical Engineering Department, Rensselaer Polytechnic Institute, Troy, N. Y.

Volume-change-of-mixing data are reported for the acetone-dichloromethane and methyl acetate–dichloromethane systems at 25° and 30° C. These data together with data from the literature provide a basis for comparison of both ΔV and ΔH for several related systems.

THIS paper reports the results of measurements (*4*) of volume changes of mixing for the binary liquid systems acetone-dichloromethane and methyl acetate–dichloromethane. Data were taken at 25° and 30° C. with a dilatometer that has previously been described (*6*), and are listed in Table I. The measurements were made at atmospheric pressure in a bath controlled to ±0.001° C. The data are believed to be accurate to within ± 1%.

The results at 25° C. are correlated by the following equations, where ΔV is in cubic centimeters per gram mole and x is mole fraction.

For acetone (1)-dichloromethane (2) at 25° C.:

$$\frac{\Delta V}{x_1 x_2} = 0.5118 - 0.0678x_1 + 0.1964x_1^2$$

For methyl acetate (1)–dichloromethane (2) at 25° C.:

$$\frac{\Delta V}{x_1 x_2} = 1.2672 - 0.0771x_1$$

The root mean-square deviations of the data points from these correlations are less than 0.5%.

A comparison of the data at 30° C. with those at 25° C. reveals that ΔV decreases with increasing temperature for acetone-dichloromethane, whereas it shows the opposite trend for methyl acetate–dichloromethane. To a first approximation $d(\Delta V/x_1x_2)/dT$ is -0.01 fo acetone-dichloromethane and $+0.005$ for methyl acetate–dichloromethane between the temperatures of 25° and 30° C.

Heats of mixing for these same systems (and from the same lots of the components) were reported by Winterhalter and Van Ness (*7*). In addition, ΔV and ΔH data are available in the literature for the acetone–carbon tetrachloride (*1, 2*) and acetone-chloroform (*3, 5*) systems. The ΔV and ΔH curves for all four systems, shown in Figure 1, allow some interesting comparisons.

Note first that the ΔV curves for acetone-CCl_4 and acetone-$CHCl_3$ are quite similar, skewed, and mostly negative. On the other hand, the ΔH curves for these systems are very different. The acetone-CCl_4 system gives relatively small positive values of ΔH (endothermic), while for acetone-$CHCl_3$, ΔH has large negative values (exothermic). For the acetone-CH_2Cl_2 system ΔV becomes entirely positive and symmetrical. ΔH is negative with values less than half those for acetone-$CHCl_3$. Comparison of the methyl acetate-CH_2Cl_2 and acetone-CH_2Cl_2 systems shows that although the ΔH curves are very close the ΔV values for methyl acetate are more than twice those for acetone.

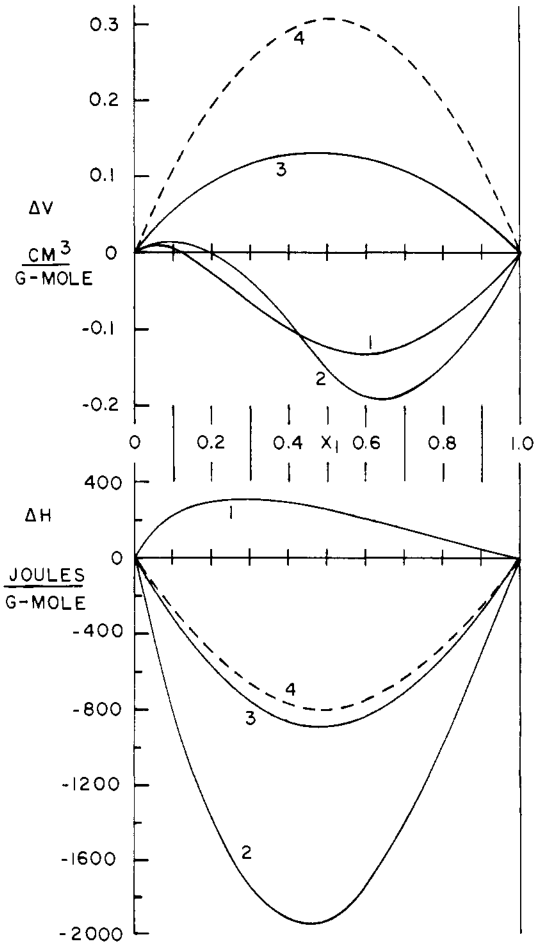
The heats of mixing should reflect the strengths of the intermolecular forces, and no doubt the negative heats exhibited by the systems containing $CHCl_3$ and CH_2Cl_2

---

[1] Present address: Esso Engineering, Florham Park, N. J.

Table I. Volume Changes of Mixing in Cubic Centimeters per Gram Mole

Dichloromethane(1)–Acetone(2)				Dichloromethane(1)–Methyl Acetate(2)			
25° C.		30° C.		25° C.		30° C.	
x_1	ΔV	x_1	ΔV	x_1	ΔV	x_1	ΔV
0.0529	0.0313	0.0993	0.0495	0.1427	0.1469	0.0365	0.0426
0.0776	0.0442	0.1409	0.0656	0.1908	0.1862	0.0711	0.0805
0.1231	0.0650	0.1789	0.0786	0.2335	0.2164	0.1319	0.1427
0.1642	0.0812	0.2141	0.0886	0.2727	0.2404	0.1851	0.1868
0.2021	0.0942	0.2617	0.0997	0.3222	0.2649	0.2334	0.2202
0.2515	0.1072	0.3028	0.1073	0.3660	0.2824	0.2753	0.2456
0.2949	0.1163	0.3398	0.1120	0.4042	0.2937	0.3313	0.2733
0.3348	0.1229	0.3838	0.1164	0.4486	0.3025	0.3778	0.2925
0.3809	0.1282	0.4220	0.1188	0.5071	0.3073	0.4187	0.3024
0.4215	0.1309	0.4559	0.1197	0.5542	0.3047	0.4655	0.3091
0.4565	0.1320	0.4645	0.1207	0.5871	0.2995	0.5139	0.3100
0.4892	0.1317	0.4930	0.1193	0.6241	0.2903	0.5625	0.3074
0.4944	0.1318	0.5078	0.1201	0.6574	0.2795	0.6067	0.2981
0.5316	0.1300	0.5366	0.1188	0.6951	0.2640	0.6414	0.2888
0.5399	0.1297	0.5370	0.1175	0.7360	0.2425	0.6803	0.2747
0.5756	0.1270	0.5684	0.1163	0.7691	0.2216	0.7236	0.2544
0.5827	0.1259	0.6043	0.1130	0.8065	0.1946	0.7602	0.2335
0.6118	0.1226	0.6348	0.1094	0.8484	0.1597	0.8013	0.2054
0.6517	0.1172	0.6682	0.1051			0.8472	0.1669
0.6983	0.1082	0.7049	0.0981			0.8984	0.1186
0.7283	0.1013	0.7461	0.0891			0.9368	0.0777
0.7618	0.0921	0.7925	0.0769			0.9780	0.0272
0.7984	0.0812	0.8263	0.0661				
0.8385	0.0675	0.8638	0.0545				
		0.9499	0.0226				



← Figure 1. ΔV and ΔH vs. composition

First named material is component 1: (1) acetone–carbon tetrachloride; (2) acetone-chloroform; (3) acetone–dichloromethane; (4) methyl acetate–dichloromethane. All curves of ΔV are for 25° C. For ΔH, curve (1) is for 45°, (2) for 25°, (3) and (4) for 30° C.

result from hydrogen bonding between the unlike molecules. The volume changes are much more difficult to relate directly to intermolecular forces. The simplest explanation is that these forces promote molecular orientations that "pack" more or less readily.

ACKNOWLEDGMENT

This work was supported in part by National Science Foundation Grant GP-2199.

LITERATURE CITED

(1) Brown, I., Fock, W., *Australian J. Chem.* **10,** 417 (1957).
(2) Brown, I., Smith, F., *Ibid.*, **15,** 9 (1962).
(3) Hubbard, J. C., *Phys. Rev.* **30,** 740 (1910).
(4) Machado, R. L., M.Ch.E. thesis, Rensselaer Polytechnic Institute, Troy, N. Y., 1965.
(5) Morcom, K. W., Travers, D. N., *Trans. Faraday Soc.* **61,** 230 (1965).
(6) Pardo, F., Van Ness, H. C., J. Chem. Eng. Data **10,** 163 (1965).
(7) Winterhalter, D. R., Van Ness, H. C., *Ibid.*, **11,** 189 (1966).

Received for review August 10, 1966. Accepted November 14, 1966.