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Joule–Thomson Coefficients of Hydrogen and Methane Mixtures

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Joule–Thomson coefficients for two mixtures of methane and hydrogen gas with hydrogen/methane compositions of 0.127/0.873 mole fraction and 0.5657/0.4343 mole fraction were measured over a pressure range of 135.83–21.39 atm and a temperature range of 294.87–274.38 K. Four experimental isenthalps were generated for each mixture and the data were compared to the predicted values from the original Redlich–Kwong equation of state, with the Soave modification and with the Prausnitz modification, and with the Peng–Robinson equation of state. All the models agree well for the methane-rich mixture, with the Peng–Robinson having the lowest deviation of 3.11%. Agreement for the hydrogen-rich mixture over the entire range was found to be nonsystematic, although all the equations showed small deviations for the high-pressure region. The Peng–Robinson equation showed the lowest overall deviation of 3.21%.

I. Introduction

Joule–Thomson coefficients are sensitive to small deviations in temperature and pressure, and because of this they are quite useful as a measure of the applicability of equations of state and correlations to a certain system. The pure components of methane and hydrogen have been studied extensively. However, mixture data for this system are noticeably absent from the literature. Hydrogen and methane are comparatively simple molecular gases at normal temperatures, but the quantum interaction of the hydrogen in the mixture causes effects that are usually not predicted well by most equations of state. The correlation of the Joule–Thomson coefficient of the mixtures to the values predicted from an equation of state gives a rough measure of these quantum effects. Better equation of state parameters could be derived by using correlations of real data.

This investigation produces data from the region close to the saturation curve and strives to correlate the data to the Redlich–Kwong and Peng–Robinson equations of state. A number of mixing rules and modifications were used to represent the theoretical treatment. The objective is to find the best equation of state and mixing rule by correlating experimental coefficients to various models, so that this equation and mixing rule combination could be used to predict other thermodynamic functions for these mixtures.

Joule–Thomson experimentation began in the late 19th century utilizing a porous plug apparatus. Hoxton (*1*) reviews the developments of this era. The first reliable data were produced by Roebuck (*2*); later Johnston (*3*) used a valve arrangement to produce data and it was this valve that was improved and modified by Ahlert (*4*). Ahlert's apparatus was used in the current work without significant modification.

II. Theoretical Development

The definition of the Joule–Thomson coefficient (μ) is

$$-(\partial T/\partial P)_H = (1/C_p)[V - T(\partial V/\partial T)_p]$$

Table I. Parameters Used in the Equation of State Models[a]

	T_c, K	P_c, atm	a	b	ω
CH_4	190.65	45.4	0.4278	0.0867	0.013
H_2	43.6	20.2	0.4278	0.0867	0.000

$K_{ij} = 0.03$; $\delta_{ij} = 0.14844$; $R = 82.057$ atm·cm^3/(g mol K)

Ideal Heat Capacity[b]

	A	10^2B	10^6C	10^9D
CH_4	4.598	1.245	2.860	−2.703
H_2	6.483	0.2215	−3.298	1.826

[a] Data from Reid et al. (*9*) and Gunn (*10*). [b] $C_p^\circ = A + BT + CT^2 + DT^3$ cal/(g mol K); T, K.

The equations of state that are applied in this work are the original Redlich–Kwong (*5*), the Redlich–Kwong with the Soave modification (*6*), and the Peng–Robinson (*7*). The mixing rules applied were the original Redlich–Kwong and Chueh and Prausnitz (*8*) ones. Gas constants for the equations were obtained from Reid et al. (*9*) and Gunn (*10*). The derivation of the heat capacity equations and the Joule–Thomson expressions for these equations of state are supplied in the Appendix.

Gunn (*10*) and his co-workers proposed a temperature dependence on the critical properties for quantum gases. These dependencies employed a correction utilizing the system temperature and molecular weight of the quantum gas:

$$T_c = T_c^\circ/[1 + (c_1/mT)] \qquad c_1 = 21.8 \text{ K}$$

$$P_c = P_c^0/[1 + (c_2/mT)] \qquad c_2 = 44.2 \text{ K}$$

The corrections were used in the calculations except for the original Redlich–Kwong values. A list of the parameters used in the equations of state are supplied in Table I.

Equation constants were calculated by using the standard methods as prescibed in the original literature. The Peng–Robinson delta (δ_{ij}) parameter, used in the intermolecular interaction cross-coefficient constant a_{ij}, was calculated by using P-V-T data that were obtained from Mueller, Leland, and Kobayashi (*11*).

III. Experimental Apparatus and Procedure

A storage tank of 2 ft^3 held the experimental mixture. The mixture was mixed from the pure components supplied by Air Products and Chemicals, Inc. Both components were at 99.97% purity, with the impurity being predominantly nitrogen. From the storage tank, the gas was fed to a two-stage intercooled Corblin oil-driven diaphragm compressor that has a maximum discharge pressure of 3600 psi. Exiting the compressor, the gas passed through a drier that contained Linde molecular sieve Type 3A. No components were absorbed by the drier; however, the drier tended to dampen the pressure oscillations that occurred from the staging of the compressor. After leaving the drier, the gas passed through a countercurrent coil-wound heat exchanger in which the hot high-pressure gas was cooled by the low-pressure stream exiting from the JT valve. The gas then flowed through a constant temperature bath which brought the gas to the desired inlet temperature. The bath consisted of a 2-gal Dewar in which Freon-11 was used as the fluid. The coolant was liquid nitrogen, used both directly and through a coil immersed in the Freon. Heat was supplied by a resistance immersion blade. The temperature

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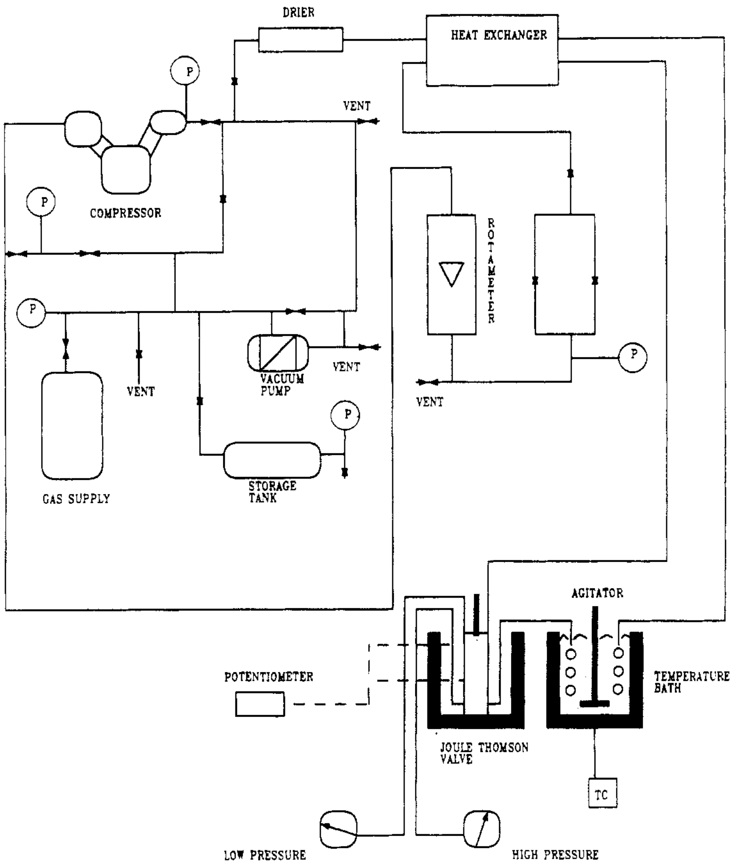

Figure 1. Flow plan of apparatus.

control was maintained by a Bayley precision controller which adjusted the heater blade temperature as required.

Bath agitation was maintained by a Fisher variable speed stirrer or by vaporization of the liquid nitrogen.

After the constant temperature bath, the gas was transferred to the JT valve by a heavily insulated copper tube. The valve was enclosed in a Dewar packed with copious amounts of a variety of insulating materials. From either side of the valve, there is a pressure tap and a Conax gland for the thermocouples. Temperature measurement was done using a Leeds and Northrop K3 potentiometer and galvanometer with calibrated copper–constantan thermocouples. Exiting the valve, the gas passed through the heat exchanger, regulating valves and flow meter, and then finally back to the low-pressure inlet of the compressor to repeat the cycle. A flow diagram of the system used is shown in Figure 1.

The system was started and after the pressure was about 100 psi greater than that desired for the experiment, system flow regulating valves were adjusted so as to get the proper test pressure. The entire system was then allowed to equilibrate and usually did so in under 3 h. Equilibrium was determined when the system pressure did not vary more than 5 psi and the temperature not more than 2.0 K over a period of 30 min. At this point the JT valve was partially closed so as to get approximately a 100 psi pressure drop from the high to low sides. After closing, the system was allowed to equilibrate again and usually did so in about an hour. During this time the inlet temperature and pressure were held constant, and after equilibrium was established the temperature and pressure were recorded. Closing the valve further yielded another data point, and this procedure was repeated five to seven times to generate the experimental isenthalp. Occasionally, the valve could not be closed very far because the temperature drop was sufficient to cause a two-phase condition. This condition was shown by the oscillation of the pressure while the temperature remained constant. When this effect occurred, the datum poin was not used and other data were taken. Only when there was complete confidence that a truly single vapor phase existed was a datum point taken as accurate.

Table II. Nitrogen Isenthalp for 294.87 K and 135.83 atm

press., atm	temp, K				
	this work	Ahlert	Din	Strobridge	Roebuck
135.83	294.88	294.90	298.84	294.99	
107.59	291.21	291.21	291.06	291.54	
82.84	287.21	287.44	287.11	287.93	
73.59	285.93	285.81	285.48	286.43	
62.17	283.37	283.76	283.33	284.45	283.76
44.92	280.03	280.20	279.82	281.18	280.31
31.58	277.09	277.37	276.93	278.43	277.33
21.39	274.93	275.00	274.54	276.48	274.91
0.00	269.55	269.58	269.25	271.04	269.33

Gas samples for later analysis were taken before and after each experimental run. Analysis was done on a Perkin Elmer 910 gas chromatograph with a 12-ft, 0.25-in.-o.d. stainless steel column packed with Chromasorb. A strip chart recorder with integrator was used to record the output from a thermal conductivity detector. The method of analysis was obtained from the U.S. Bureau of Mines report (*12*).

IV. Results and Discussion

The system was checked for enthalpy leakage by making an initial determination of an isenthalp with pure nitrogen. Nitrogen was selected since there are reliable data for the Joule–Thomson coefficients by many investigators. Table II shows the comparison between the isenthalp generated by using recorded data values and isenthalps reported by others. As can be seen, the temperatures are reliably reproduced, showing that our method agrees with the previous data for nitrogen. By using our data and fitting it to a third order polynominal, we can then differentiate this polynomial to yield the coefficients in Table III that, again, agree well to the reported values.

Table III. Joule-Thomson Coefficients for Nitrogen Isenthalp

press., atm	coefficient K, atm: this work	Ahlert	Din	Strobridge	Roebuck
135.83	0.110	0.116	0.119	0.110	
107.59	0.143	0.142	0.147	0.134	
82.84	0.172	0.167	0.173	0.158	
73.17	0.183	0.177	0.182	0.167	
62.17	0.196	0.190	0.194	0.180	0.189
44.92	0.216	0.210	0.212	0.199	0.213
31.58	0.231	0.227	0.226	0.215	0.231
21.39	0.243	0.240	0.237	0.227	0.246
0.00	0.271	0.268	0.259	0.254	0.276

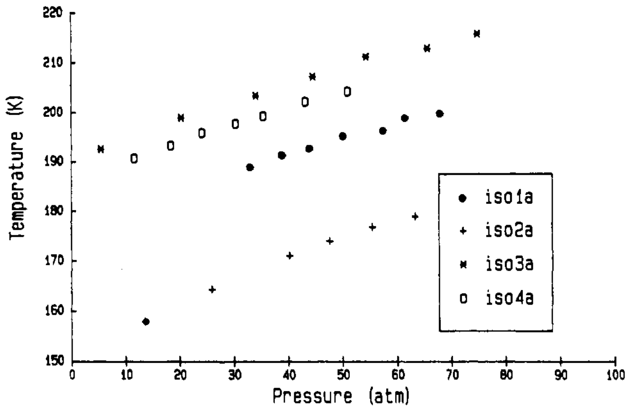

Figure 2. Mixture A isenthalps.

This method of fitting the isenthalp data to a polynomial, where the Joule-Thomson coefficient can then be obtained from differentiation, is quite stable provided that the order of the polynomial is much less that the number of datum points. We generate at least eight datum points and we fit the data using a third-order polynomial. Terms of higher order were found to contribute less than 0.5% to the final result and were quickly monotonically decreasing. The three parameters were found by minimization in the least-squares sense where the error for the least squares was less than 0.1% of the parameter value. Fitting data to a low-order polynomial, especially when the derivative of the data is necessary, is a well-established stable numerical procedure. While there are other methods, such as differentiating the data to obtain the coefficients, the polynomials are useful since they can be explicitly differentiated for the range of pressure and temperature for each isenthalp.

Table IV and Figures 2 and 3 show the isenthalps for the two experimental mixtures A and B. One can see from the graphs of the isenthalps that the data present smooth curves and the subsequent differentiation to obtain the Joule-Thomson coefficients yields interesting results.

Table V and Figure 4 show the coefficients for the hydrogen-rich mixture. For this mixture, the data fall on both sides of the predicted values. None of the equations yields a very good correlation in all pressure ranges; however, at higher pressures the agreement is better than at low. This leads to the belief that the equations overcorrect for the quantum interaction at low pressure. The error associated with the hydrogen-rich mixtures are 8.72% for the original Redlich-Kwong equation, with a range of −17.50 to 1.38; 4.21% for the Prausnitz modification, with a range of −9.24 to 9.33; 4.89% for the Soave modification, with the range of −1.86 to 16.25; and for the Peng-Robinson equation 3.21% with a range of −1.18 to 11.38. The run 3a is in doubt because of high error, but is reported.

Table IV. Experimental Isenthalps

press., atm	temp, K	press., atm	temp, K
Mixture A 0.5657/0.4343 mole fraction Hydrogen/Methane			
1A			
68.03	199.54	43.89	192.59
61.57	198.68	38.82	191.21
57.47	196.09	33.00	188.85
50.15	194.96		
2A			
71.43	181.63	40.15	170.96
63.27	178.71	25.85	164.19
55.45	176.62	13.53	157.87
47.62	173.86		
3A			
74.83	215.25	34.02	203.22
65.66	212.43	20.33	198.85
54.42	210.85	5.45	192.58
44.56	206.97		
4A			
51.02	204.00	24.15	195.72
43.21	202.00	18.37	193.17
35.38	199.12	11.57	190.62
30.28	197.61		
Mixture B 0.127/0.873 mole fraction Hydrogen/Methane			
1B			
66.33	219.44	44.23	200.88
59.20	213.48	40.84	197.53
51.24	208.68	34.01	190.31
47.62	204.03		
2B			
47.64	198.22	20.48	167.72
41.26	192.64	13.76	155.92
34.77	185.08	3.40	133.57
27.14	178.74		
3B			
54.43	220.18	31.30	200.50
50.01	216.91	25.51	193.31
44.23	211.72	18.64	185.52
38.79	207.55		
4B			
71.43	245.60	30.97	215.06
62.93	238.20	19.41	203.07
54.43	235.33	5.11	182.98
42.18	227.38		

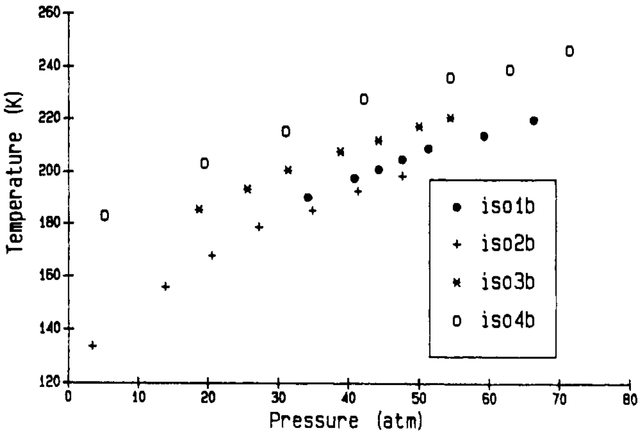

Figure 3. Mixture B isenthalps.

Table VI and Figure 5 show the Joule-Thomson coefficients for the four runs of the approximate 50/50 mixture. The Peng-Robinson curves correlate quite closely with the data, while the general trend is that as one goes from the original Redlich-Kwong equation of state to the Prausnitz modification to the Soave modification and finally to the Peng-Robinson equation, the agreement between prediction and data improves. The methane-rich mixture showed, overall, excellent agreement.

Table V. Mixture A Joule-Thomson Coefficients (K, atm) for 0.5657/0.4343 mole fraction Hydrogen/Methane[a]

data	RK	dev, %	RP	dev, %	RS	dev, %	PR	dev, %
Run 1A								
0.2617	0.2871	-9.73	0.2674	-2.21	0.2461	5.96	0.2512	3.98
0.2715	0.3019	-11.19	0.2816	-3.73	0.2597	4.33	0.2661	1.99
0.2807	0.3180	-13.29	0.2969	-5.79	0.2747	2.13	0.2812	-0.18
0.3023	0.3365	-11.30	0.3148	-4.13	0.2922	3.32	0.3004	0.63
0.3264	0.3580	-9.67	0.3354	-2.77	0.3127	4.18	0.3221	1.32
0.3496	0.3740	-6.97	0.3509	-0.37	0.3283	6.10	0.3390	3.05
0.3805	0.3964	-4.18	0.3725	2.09	0.3502	8.00	0.3622	4.81
Run 2A								
0.2846	0.3310	-16.29	0.3080	-8.23	0.2867	-0.75	0.2843	0.09
0.3094	0.3623	-17.11	0.3377	-9.16	0.3151	-1.86	0.3130	1.19
0.3383	0.3921	-15.90	0.3661	-8.21	0.3425	-1.23	0.3414	-0.91
0.3723	0.4267	-14.60	0.3991	-7.19	0.3726	-0.62	0.3746	-0.61
0.4095	0.4633	-13.13	0.4342	-6.01	0.4091	-0.10	0.4105	-0.22
0.4937	0.5480	-11.02	0.5156	-4.45	0.4900	0.75	0.4949	-0.26
0.5797	0.6345	-9.46	0.5993	-3.37	0.5733	1.11	0.5835	-0.65
Run 3A								
0.2018	0.2371	-17.50	0.2204	-9.24	0.1998	0.96	0.2084	-3.29
0.2404	0.2575	-7.10	0.2400	0.19	0.2187	9.03	0.2284	5.02
0.2834	0.2793	1.46	0.2610	7.91	0.2393	15.56	0.2512	11.38
0.3171	0.3069	3.22	0.2875	9.53	0.2657	16.21	0.2792	11.93
0.3490	0.3375	3.30	0.3171	9.14	0.2956	15.31	0.3117	10.69
0.3841	0.3786	1.43	0.3571	7.03	0.3367	12.34	0.3574	6.95
0.4140	0.4340	-4.83	0.4111	0.70	0.3931	5.06	0.4200	-1.45
Run 4A								
0.2735	0.3051	-11.55	0.2854	-4.35	0.2634	3.70	0.2742	-0.25
0.3001	0.3255	-8.48	0.3051	-1.68	0.2831	5.66	0.2957	1.46
0.3268	0.3501	-7.15	0.3289	-0.64	0.3070	6.06	0.3215	1.62
0.3442	0.3654	-6.17	0.3437	0.13	0.3221	6.41	0.3382	1.74
0.3652	0.3847	-5.35	0.3625	0.74	0.3414	6.50	0.3596	1.53
0.3850	0.4069	-5.69	0.3841	0.25	0.3636	5.56	0.3838	0.31
0.4084	0.4321	-5.80	0.4086	-0.05	0.3892	4.71	0.4123	-0.95

[a] RK, RP, RS, and PR are values predicted by Redlich-Kwong, Redlich-Kwong-Prausnitz, Redlich-Kwong-Soave, and Peng-Robinson equations of state.

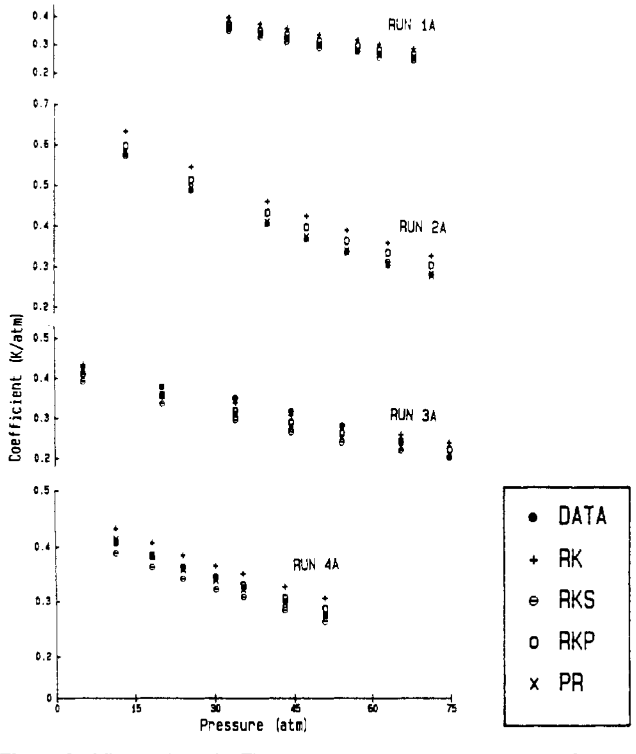

Figure 4. Mixture A Joule-Thomson coefficients, where RK, RKS, RKP, PR are respectively the Redlich-Kwong, Redlich-Kwong-Soave, Redlich-Kwong-Prausnitz, and Peng-Robinson equations of state.

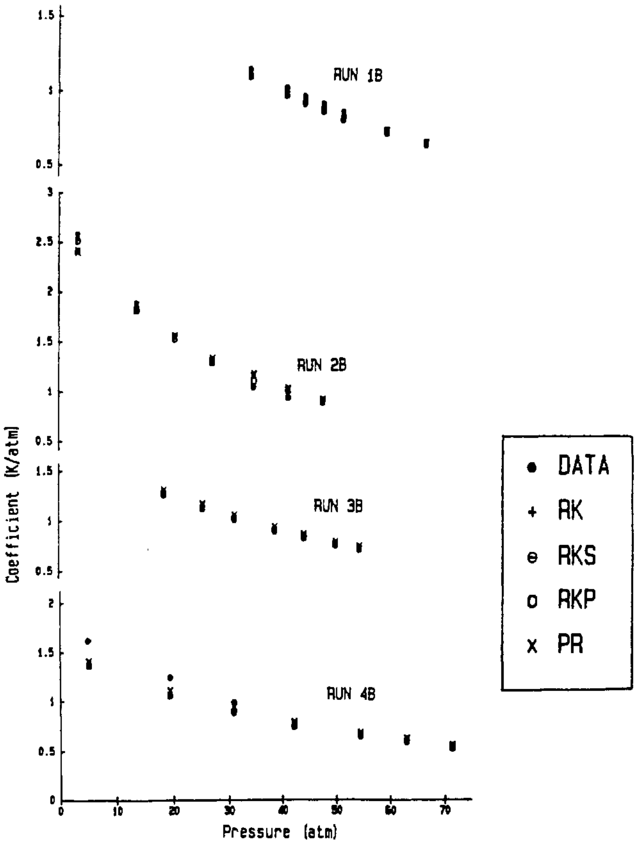

Figure 5. Mixture B Joule-Thomson coefficients, where RK, RKS, RKP, PR are respectively the Redlich-Kwong, Redlich-Kwong-Soave, Redlich-Kwong-Prausnitz, and Peng-Robinson equations of state.

There is a clear pattern that as one progresses to a later equation or modification, the correlation is improved. The Peng-Robinson equation does an excellent job of prediction,

Table VI. Mixture B Joule–Thomson Coefficients (K, atm) for 0.127/0.873 mole fraction Hydrogen/Methane[a]

data	RK	dev, %	RP	dev, %	RS	dev, %	PR	dev, %
				Run 1B				
0.6757	0.6634	1.81	0.6570	2.76	0.6786	−0.44	0.6653	1.54
0.7648	0.7401	3.22	0.7328	4.18	0.7563	1.10	0.7426	2.89
0.8753	0.8274	5.47	0.8190	6.43	0.8448	3.48	0.8328	4.89
0.9296	0.8864	4.64	0.8774	5.61	0.9050	2.64	0.8923	4.01
0.9826	0.9375	4.59	0.9280	5.56	0.9570	2.61	0.9447	3.86
1.0378	0.9932	4.29	0.9831	5.27	1.0136	2.33	1.0018	3.47
1.1553	1.1200	3.05	1.1087	4.04	1.1419	1.16	1.1316	2.05
				Run 2B				
0.9218	0.9225	−0.04	0.9129	0.97	0.9417	−2.15	0.9251	−0.35
0.9542	1.0318	−8.12	1.0212	−7.02	1.0530	−10.34	1.0368	−8.65
1.0590	1.1710	−10.58	1.1158	−9.43	1.1939	−12.74	1.1780	−11.23
1.2744	1.3209	−3.64	1.3076	−2.59	1.3422	−5.40	1.3317	−4.49
1.5441	1.5516	−0.48	1.5363	0.50	1.5689	−1.60	1.5572	−0.85
1.8935	1.8410	−2.77	1.8238	3.68	1.8380	2.93	1.8278	3.47
2.5841	2.5424	−1.62	2.5211	2.44	2.4081	6.81	2.4054	6.92
				Run 3B				
0.7476	0.7388	1.18	0.7313	2.18	0.7539	−0.84	0.7475	0.02
0.7814	0.7849	−0.45	0.7770	0.57	0.8009	−2.49	0.7955	−1.80
0.8404	0.8558	−1.82	0.8472	−0.80	0.8731	−3.89	0.8690	−3.40
0.9112	0.9219	−1.17	0.9128	−0.17	0.9404	−3.19	0.9387	−3.01
1.0331	1.0319	0.12	1.0219	1.08	1.0511	−1.74	1.0529	−1.92
1.1464	1.1439	0.22	1.1331	1.16	1.1624	−1.39	1.1667	−1.77
1.3029	1.2814	1.65	1.2698	2.54	1.2947	0.63	1.3043	−0.11
				Run 4B				
0.5467	0.5406	1.12	0.5351	2.13	0.5505	−0.69	0.5493	−0.47
0.5838	0.6062	−3.83	0.6000	−2.78	0.6176	−5.78	0.6167	−5.64
0.6506	0.6575	−1.07	0.6510	−0.06	0.6698	−2.96	0.6727	−3.39
0.7989	0.7577	5.15	0.7504	−6.07	0.7722	−3.34	0.7802	−2.34
0.9886	0.8996	9.01	0.8911	9.86	0.9160	7.34	0.9282	6.11
1.2381	1.0646	14.01	1.0553	14.77	1.0787	12.88	1.0990	11.24
1.6226	1.3791	15.00	1.3681	15.68	1.3672	15.74	1.4020	13.59

[a] RK, RP, RS, and PR are values predicted by Redlich–Kwong, Redlich–Kwong–Prausnitz, Redlich–Kwong–Soave, and Peng–Robinson equations of state.

especially in the higher pressure region. The errors associated with this mixture are 3.89% for the Redlich–Kwong with a range of −10.00 to 15.00, 3.89% for the Prausnitz modification with a range of −9.43 to 15.68; 3.33% for the Soave modification with a range of −10.43 to 15.74; and 3.11% for the Peng Robinson with a range of −11.23 to 13.59.

It is believed that with the methane-rich mixture all the equations do a good job of prediction because the quantum interaction is so slight; however, the hydrogen-rich mixture causes problems since the equations all undercorrect at low pressure, then overcorrect at high pressure. This would seem to be the case, since the quantum effects would be functions of not only temperature, by a kinetic energy approach, but also pressure by a molecular radii concept. The ω parameter in the Prausnitz modification takes into account the critical properties in its definition, but most correlations that use this to obtain other parameters are only weak functions of ω. It is believed that better correlations could be obtained if reduced properties were used to formulate the empirical constants.

Agreement with the results of Eakin et al. (*13*) is poor. They do not report the coefficients; one had to differentiate their data. It was found that a 51.048/48.840 mole fraction mixture of methane/hydrogen at an inlet of 68.03 atm and −17.81 K had a coefficient of 0.19 K/atm. Extrapolation of the current work to this range yields a result of 0.265 K/atm.

Errors associated with the experimental work are due to inaccuracy in the pressure and temperature readings or calibration, and error in mixture composition. The Heise gauges, even with a reliable calibration curve, exhibit errors due to hysteresis and readability. These errors are estimated by the recommendation of the manufacturer to be 0.2 atm and result in an error in the Joule–Thomson coefficients on the order of 0.4%. The platinum resistance thermometer used for calibration of the thermocouples gave a temperature error in the thermocouples of 0.014 K. This error caused an error in the Joule–Thomson coefficient of 0.02%. These temperature and pressure errors are, unfortunately, unavoidable. While there is approximately 2% error in the data reduction, the polynomial technique has proved to be quite stable. This error may change the values of the coefficients somewhat but not the assessment of the viability of a particular equation of state.

The errors associated with composition are due to the method of mixture analysis. By statistical determination of redundant samples, the error associated with the integrator on the gas chromatograph was estimated at 0.5%. This error lead to a 0.3% error in the composition determinations.

In conclusion, we have investigated the viability of a number of equations of state by using the Joule–Thomson coefficient as a sensitive measure of an equation's ability to model two hydrocarbon mixtures. We find that for a methane-rich mixture, all the equations model the data region well, with the most chronologically advanced equation preforming the best overall.

For the hydrogen-rich mixture, there is more deviation from the equations and the data. We believe this is due in part to the over- and undercorrection of the quantum interaction terms and suggest that the terms should be functions of reduced properties. This would take into account the pressure and temperature range of interest.

Appendix

Expressions for Heat Capacity and Joule–Thomson Coefficient. For the Redlich–Kwong equation of state

$$p = \frac{RT}{V - b} - \frac{a}{T^{0.5}V(V + b)}$$

$$C_p - C_p{}^\circ = \left[\frac{-RT}{V-b} - \frac{0.5a}{T^{0.5}(V+b)V} + \frac{RTV}{(V-b)^2} - \frac{2a}{T^{0.5}(V+b)^2} - \frac{ab}{T^{0.5}(V+b)^2V}\right]\left[-\frac{RT}{(V-b)^2} + \frac{2a}{T^{0.5}(V+b)^2V} + \frac{ab}{T^{0.5}V^2(V+b)^2}\right]^{-1}$$

The parameter *a* is a function of temperature.

$$a(T)_{\mathrm{m}} = \sum\sum y_iy_j(1 - K_{ij})(a_{ci}a_{ci}a_i(T)\ a_j(T))^{0.50}$$

$$a_{ci} = 0.42747R^2T_{ci}{}^2/P_{ci}$$

$$a_i(T) = (1 + (m_i(1 - T_{ri}{}^{0.5})))^2$$

$$m_i(\omega) = 0.480 + 1.57\omega_i - 0.176\omega_i{}^2$$

$$\frac{\partial P}{\partial T} = R/(V-b) + 0.5T^{-1.5}(V(V+b))^{-1}\frac{\partial a_{\mathrm{m}}(T)}{\partial T}$$

We can express the derivative of $a_{\mathrm{m}}(T)$ as ZQ

$$Z = \sum\sum y_iy_j(1 - K_{ij})(a_{ci}a_{cj})^{0.5}$$

$$Q = -0.5(m_i + m_im_j)(T_{ci}T)^{-0.5} - 0.5(m_j + m_im_j)(T_{cj}T)^{-0.5} + m_im_j(T_{ci}T_{cj})^{-0.5}$$

$$\mathrm{DPDT} = \frac{\partial P}{\partial T} = R/(V-b) - (ZQ)/(V(V+b))$$

$$\mathrm{DPDV} = \frac{\partial P}{\partial V} = \left(\frac{-RT}{(V-b)^2} + \frac{a_{\mathrm{m}}}{T^{0.5}(V(V+b)^2)}\right)(2V+b)$$

$$\mathrm{D2PDT2} = \frac{\partial^2 p}{\partial T^2} = Z\,\mathrm{DQ}/(V(V+b))$$

$$\mathrm{DQ} = \frac{\partial Q}{\partial t} = 0.25(m_i + m_im_j)(T_{ci}{}^{-0.5}T^{-1.5}) + 0.25(m_j + m_im_j)(T_{cj}{}^{-0.5}T^{-1.5})$$

$$C_p = C_p{}^\circ - R - T(\mathrm{D2PDT2})(\mathrm{DPDV})^{-1} - (\mathrm{TZ(DQ)}/b)(\ln((V+b)/V)$$

$$\mu = \frac{(-T(\mathrm{DPDT}) - V(\mathrm{DPDV}))}{C_p(\mathrm{DPDV})}$$

A similar result for the Peng-Robinson equation of state:

$$P = \frac{RT}{V-b} - \frac{a}{b(V-b)V(V+b)}$$

$$\mathrm{DPV} = \frac{\partial P}{\partial V} = \frac{-RT}{(V-b)^2} + \frac{2a(V+b)}{(V(V+b) + (V-b)b)^2}$$

$$\mathrm{DPT} = \frac{\partial P}{\partial T} = \frac{R}{(V-\mathrm{b})^2} - (V + (V+b) + b(V-b))^{-1}\frac{\partial a}{\partial T}$$

$$a = \sum\sum y_iy_ja_{ij}$$

$$a_{ij} = a_{ci}a'_i \qquad (i = j)$$

$$a_{ij} = C(a_{ii}a_{jj})^{0.5} \qquad (i \neq j)$$

where

$$C = (1 - \delta_{ij})^{0.5}$$

$$a_{cii} = 0.45724(RT_{ci})^2/P_{ci}$$

$$a'_i = (1 + K_i(1 - T_{ri}{}^{0.5}))^2$$

$$K_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i{}^2$$

$$\frac{\partial a_{ij}}{\partial T} = \mathrm{D}a_{ij} =$$

$$a_{cii}\mathrm{D}a'_i = -K_i((a_{cii}a'_i)^{0.5})(T_{ci}T)^{-0.5} \qquad (i = j)$$

$$= 0.5(a_{cii}a_{cij})^{-0.5}C(a'_j\mathrm{D}a'_i + a'_i\mathrm{D}a'_j)(a'_ia'_j)^{-0.5} \qquad (i \neq j)$$

$$\mathrm{D}a'_i = -[(a'_iK_i)/(T_{ci}T)]^{0.5}$$

$$Q = \sum\sum y_iy_j\mathrm{D}a_{ij}$$

$$\mathrm{DPT} = \frac{\partial P}{\partial T} = \left(\frac{R}{V-b}\right) - (V(V+b) + b(V-b))^{-1}Q$$

$$\mathrm{D2PT} = \frac{\partial^2 P}{\partial T^2} = -(V(V+b) + b(V-b))^{-1}\frac{\partial Q}{\partial T}$$

$$\mathrm{DQ} = \frac{\partial Q}{\partial T} = \sum\sum y_iy_j\frac{\partial^2 a_{ij}}{\partial T^2} = \sum\sum y_iy_j\mathrm{D2}a_{ij}$$

$$\mathrm{D2}a_{ii} = ac_{ij}\mathrm{D2}a'_i$$

$$\mathrm{D2}a_{ij} = a_{cij}\left(\frac{k_ia'_i{}^{0.5}}{T_{ci}{}^{0.5}}\right)\left(\frac{0.5}{T^{1.5}} - \frac{K_i}{T_{ci}{}^{0.5}T^{1.5}}\right) \qquad (i = j)$$

$$\mathrm{D2}a_{ij} = (0.5)[(a'_ia'_j)^{-0.5}(a'_j\mathrm{D2}a_{ii} + 2\mathrm{D}a'_i\mathrm{D}a'_j + a'_i\mathrm{D2}a'_{jj}) + (a'_j\mathrm{D}a'_i + a'_i\mathrm{D}a'_j) - 0.5(a'_ia'_j)^{-1.5}(a'_i\mathrm{D}a'_j + a'_i\mathrm{D}a'_j)] \qquad (i \neq j)$$

Substituting into the equations we obtain:

$$C_p = C_p{}^\circ - R - T((\mathrm{DPT})^2/\mathrm{DPV}) + T(\mathrm{DQ})(8b^2)^{-0.5}\ln\left[\frac{2V + b + (8b^2)^{0.5}}{2V + b - (8b^2)^{0.5}}\right]$$

$$\mu = (-(T(\mathrm{DPT})) - (V(\mathrm{DPV}))/(C_p(\mathrm{DPV}))$$

Glossary

P	pressure
V	specific volume
T	temperature
V	volume
R	gas constant
C_p	molar heat capacity
H	enthalpy
Z	compressibility factor
a	pure component attraction interaction parameter
b	pure component hard-core interaction parameter
y	mole fraction of component y
x	mole fraction of component x
c_1,c_2	empirical constant for Cheuh T_c,P_c equations
m	molecular weight
k	Prausnitz interacting parameter

Greek Letters

ω	acentric factor
α	a dimensional factor
Ω	proportionality constant
δ	Peng-Robinson parameter

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μ	Joule–Thomson coefficient

Subscripts

c	critical property
i, j	component identification

Registry No. H_2, 1333-74-0; CH_4, 74-82-8.

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Viscosities of Binary Solvent Mixtures of *N*,*N*-Diethylmethanesulfonamide with Aliphatic Alcohols

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Viscosities were measured for binary solvent mixtures of *N*,*N*-diethylmethanesulfonamide (DEMSA) with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-methyl-2-propanol at 303.15 K and used to calculate the excess viscosities and excess Gibbs energies of activation of flow. Both excess quantities were negative over the whole composition range for all mixtures studied, except the excess Gibbs energies for mixtures containing methanol, which were positive. The values decreased with the length of the alkyl chain of the alcohol and were smaller for the secondary and tertiary alcohols than for the primary analogues.

Introduction

As part of our studies on the thermodynamic properties of binary solvent mixtures of carboxamides and sulfonamides with aliphatic alcohols we recently reported the excess enthalpies (*1*) and the excess volumes (*2*) for binary mixtures of *N*,*N*-diethylmethanesulfonamide, $CH_3SO_2N(C_2H_5)_2$, with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-methyl-2-propanol. The results were interpreted in terms of intermolecular interactions and geometrical effects in the mixtures. In continuation of this work we have now measured the viscosities of these binary mixtures at 303.15 K. The viscosities, together with the excess volumes from the earlier study (*2*), were used to calculate the excess viscosities and the excess Gibbs energies of activation of flow.

Experimental Section

Materials. The alcohols were the same as in the previous studies (*1*, *2*). *N*,*N*-Diethylmethanesulfonamide was prepared and purified as described earlier (*1*).

Measurements. Viscosities were measured with Cannon-Ubbelohde viscometers (*3*) (manufactured by Cannon Instrument Co., USA) equipped with an optoelectronic device for measuring the efflux time. Densities were available from the previous study (*2*). Viscosities are expressed in units of centipoise equal to 10^{-3} N s m^{-2}. The reproducibility in the viscosity measurements was within ±0.005 cP. The temperature of the water baths remained constant within ±0.02 K.

Table I. Viscosities η of Binary Mixtures of DEMSA with Aliphatic Alcohols at 303.15 K[a]

x	η/cP	x	η/cP	x	η/cP
		Methanol			
0	0.514	0.3717	1.234	0.6922	2.289
0.0650	0.604	0.4509	1.451	0.7686	2.636
0.1394	0.730	0.5148	1.645	0.8304	2.956
0.2155	0.884	0.5856	1.878	0.9084	3.414
0.2885	1.034				
		Ethanol			
0	0.990	0.3659	1.424	0.6622	2.217
0.0656	1.000	0.4606	1.635	0.7430	2.533
0.1402	1.067	0.5135	1.765	0.8454	3.026
0.2228	1.175	0.5968	2.002	0.9395	3.597
0.2849	1.274				
		1-Propanol			
0	1.728	0.3821	1.793	0.6850	2.461
0.0661	1.610	0.4421	1.884	0.7587	2.716
0.1423	1.583	0.5219	2.039	0.8085	2.925
0.2148	1.612	0.5944	2.204	0.8907	3.334
0.3057	1.693				
		2-Propanol			
0	1.783	0.3391	1.686	0.6857	2.433
0.0680	1.593	0.4088	1.792	0.7556	2.684
0.1441	1.544	0.4524	1.863	0.8417	3.057
0.2157	1.565	0.5136	1.984	0.9259	3.518
0.2582	1.598	0.5952	2.183		
		1-Butanol			
0	2.272	0.3626	1.985	0.6908	2.550
0.0631	2.045	0.4515	2.078	0.7579	2.742
0.1404	1.942	0.5227	2.175	0.8437	3.089
0.2197	1.918	0.6053	2.340	0.9281	3.552
0.2937	1.942				
		2-Methyl-2-propanol			
0	3.376	0.3944	2.453	0.7621	3.010
0.0764	2.857	0.4712	2.501	0.8534	3.304
0.1463	2.630	0.5369	2.579	0.9381	3.657
0.2364	2.482	0.6062	2.664	1.0	4.059
0.3171	2.437	0.6888	2.796		

[a] x is the mole fraction of DEMSA.

Results and Discussion

Measured viscosities of the pure components and mixtures are reported in Table I. The viscosities of the pure components are in good agreement with the literature values: 0.510

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