Thermodynamic Properties Prediction of Vinyl Acetate Systems at High Pressures

B. G. Shiva Prasad and Derek Woollatt
Dresser-Rand, EPCD, Painted Post, NY 14870

Vinyl acetate (a polar compound) has become a key ingredient in many industrial and consumer products. However, very little is known about its thermodynamic properties. This article presents a simple modification of Wu and Stiel's (1985) method (originally developed for predicting thermodynamic properties of polar compounds up to $P_r = 10$) for extending its range of applicability to very high pressures of the order of $P_r = 80$. The predictions show good agreement with the experimental data for specific volume in the case of vinyl acetate, and specific volume, enthalpy and entropy for mixtures of ethylene and vinyl acetate for compositions up to 50 wt. % of vinyl acetate. Further validation for other polar systems would determine if this method is applicable to polar compounds in general.

Introduction

Polymers and polyethylene have become common household names because of their growing application in day-to-day life as adhesives, paints, shoe soles, films for food packaging, etc. Vinyl acetate, a monomer with a highly active ethylenic group, can easily polymerize to form homo- or heteropolymers with other compounds like ethylene, vinyl alcohol, and acrylates.

High-pressure polymerization is one of the important techniques used for manufacturing copolymers of vinyl acetate with ethylene. This involves compressing mixtures of ethylene and vinyl acetate in varying proportions (depending on the desired product and properties) to pressures as high as 200 to 300 MPa. Hence, thermodynamic properties of these mixtures at such high pressures are needed not only for chemical process design but also for design of compressors used for compressing these gases. There are two hurdles to this. There are not many equations of state developed for such high pressures, and particularly for polar compounds like vinyl acetate, they are nonexistent. Also, vinyl acetate is a very poorly researched compound as far as thermodynamic properties are concerned. The experimental data of Kudchadker (1975), and Ratzsch and Findeisen (1980) are the only two sets of published data discovered by the authors during the course of this work. The former gives enthalpy and entropy at atmospheric pressure only, while the latter, although extending to very high pressures (400 MPa), gives only specific volume data. Further, to the authors' best knowledge, thermodynamic property data for the ethylene–vinyl acetate system at such high pressures is virtually nonexistent in public literature.

The objective of this investigation was to generate the important thermodynamic properties needed for compressor design and performance evaluation, such as specific volume, enthalpy and entropy, and to develop a method of predicting the thermodynamic properties of the ethylene–vinyl acetate system at high pressures, at least up to 400 MPa. A literature review indicated a few investigations relating to polar compounds done by Eubank and Smith (1962), Stipp et al. (1973), Halm and Stiel (1970), Kalback and Starling (1976), Nishiumi and Robinson (1981), and Wu and Stiel (1985).

Of all these, the authors readily identified the Wu and Stiel (1985) method for polar compounds, an extension of the Lee-Kesler method (1975), as the appropriate one to start with. The reason being that unlike many other older methods, it contained only linear terms (according to Wu and Stiel, linear terms are sufficient when dealing with compounds with lower acentric and polarity factors compared to water) in acentric and polarity factors to account for shape and polarity effects. However, the application of both of these methods was limited to a reduced pressure $P_r = 10$.

As a first step, the authors followed their natural instincts to just apply these methods at high pressures. The Lee-Kesler method was tried for propane and butane up to about 65 MPa, for nitrogen up to 100 MPa and ethylene up to 275 MPa. The good agreement with experimental data obtained

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Correspondence concerning this article should be addressed to B. G. Shiva Prasad.

for these cases gave the required impetus to extend the Wu and Stiel method to higher pressures. The Wu and Stiel method was initially tried for 10 and 30 wt. % of a mixture of vinyl acetate with ethylene. The mixture critical properties were determined using the method of Huang and Stiel (1987), which is an extension of the method of Maris and Stiel (1985) for determining the interaction second virial coefficients of polar mixtures from the parameters of their components. The comparison of the predicted properties with experimental data was unsatisfactory at high pressures (up to 300 MPa). Particularly for enthalpy, discrepancies up to 12%, and for entropy, much higher than that were noticed.

A simple multiplication factor applied for the compressibility factors of the simple and reference fluids made the prediction agree with experimental data reasonably well for three compositions (10, 30 and 50 wt. %) of vinyl acetate with ethylene. Also, very good agreement was obtained for the prediction of specific volume of vinyl acetate with the experimental data of Rätzsch and Findeisen up to pressures as high as 400 MPa.

Prediction Method

The method used is a simple extension of the Wu and Stiel method of predicting the thermodynamic properties of polar compounds. The Wu and Stiel method itself is an extension of the Lee-Kesler (1975) method which does not include correction for polarity effects. Both of these methods were limited in range of application to $0.3 \leq T_r \leq 4$ and $0.01 \leq P_r \leq 10$.

In the Lee-Kesler method, an equation of state in terms of reduced pressure and temperature is solved for a simple fluid ($\omega = 0$) and for a reference fluid (like *n*-octane; $\omega = 0.3978$) to determine their reduced volumes and hence compressibility factors. Then, the compressibility factor for a nonpolar compound is given by

$$Z = Z^{(0)} + \omega Z^{(1)} \tag{1}$$

Wu and Stiel (1985) applied a similar linear correction to account for polarity effects and defined Z for a polar compound as

$$Z = Z^{(0)} + \omega Z^{(1)} + Y Z^{(2)} \tag{2}$$

where Y is a constant based on the polarity factor, χ, for the compound of interest. This polarity factor, which is a measure of the magnitude of the electrostatic field in a molecule manifested as a dipole moment, could be determined from saturated liquid density or saturated vapor pressure using the equation (Wu and Stiel, 1985):

$$\chi = -\log P_{RS}]_{T_R = 0.6} + 1.7\omega + 1.552 \tag{3}$$

Y itself, for any component, i, of a mixture (or for any single compound) can be determined using

$$Y_{ij} = 1.7939\omega_{ij} + 49.2709\chi_{ij} - 68.1537\omega_{ij}\chi_{ij} + 30.7829\chi_{ij}^2 - 2.2894\omega_{ij}^2 \tag{4}$$

of Huang and Stiel (1987) with $i = j$ for a single compound.

Water was used as a second reference fluid by Wu and Stiel for determining the properties of compounds whose acentric and polarity factors are less than those of water. Since this condition was satisfied by the vinyl acetate systems being studied and the thermodynamic properties of water at high pressures can be determined with a high degree of accuracy using the equation of state of water given by Keenan et al. (1969), water was used as a reference fluid in this study as well. However, one could choose any other compound like a halocarbon as a reference fluid.

A deviation factor to account for polarity effect was determined using (Wu and Stiel, 1985):

$$Z^{(2)} = Z^{(w)} - [Z^{(0)} + 0.344 Z^{(1)}] \tag{5}$$

Following Wu and Stiel, $Z^{(w)}$ for water at the same values of P_r and T_r as for the gas was determined using the equation of state for water given by Keenan et al. (1969). Z was then determined for the required gas using Eq. 2, and the specific volume obtained from, $V = (ZRT)/P$.

For determining the enthalpies, $\Delta H^{*(0)}$ and $\Delta H^{*(r)}$ for the simple and reference fluids were computed using the Lee-Kesler method. Then the deviation factors for enthalpy to account for shape, and polarity effects were determined using,

$$\Delta H^{*(1)} = \frac{\Delta H^{*(r)} - \Delta H^{*(0)}}{\omega^{(r)}} \tag{6}$$

$$\Delta H^{*(2)} = \frac{H_w - H_w^0}{T_{c_w} R} - \Delta H^{*(0)} - \omega_w \Delta H^{*(1)} \tag{7}$$

ΔH^* and H were then obtained using

$$\Delta H^* = \Delta H^{*(0)} + \omega \Delta H^{*(1)} + Y \Delta H^{*(2)} \tag{8}$$

and

$$\Delta H^* = (H - H^0)/RT_c \tag{9}$$

The procedure for computing entropy is similar to that described above for enthalpy.

Mixing rule

The pseudocritical properties of the polar mixture were determined using the method of Huang and Stiel (1987). Their method is essentially based on the approach of Maris and Stiel (1985) for determining the interaction second virial coefficients of mixtures involving polar compounds. For this purpose, following Maris and Stiel, the interaction constants T_{c12}, P_{c12}, ω_{12}, and χ_{12} were determined from the molecular energy, distance and size parameters of the components through the following equations in addition to Eq. 4:

$$\frac{\epsilon_{12}}{kT_{c12}} = 1.0042 + 3.0454\omega_{12} - 58.883\chi_{12} + 87.1979\omega_{12}\chi_{12} + 6.8813\chi_{12}^2 - 4.2422\omega_{12}^2 \tag{10}$$

$$a_{12}^{*} = \frac{2a_{12}}{P_{0_{12}}} = 0.1501 + 2.3724\omega_{12} - 25.3457\chi_{12} + 35.7975\omega_{12}\chi_{12} - 64.3636\chi_{12}^{2} - 2.054\omega_{12}^{2} \quad (11)$$

$$\rho_{o_{12}}\left(\frac{P_{c12}}{T_{c12}}\right)^{1/3} = \frac{(1.0554 - 0.4003\omega_{12} + 10.8594\chi_{12} - 18.7859\omega_{12}\chi_{12} + 23.5418\chi_{12}^{2} - 0.0871\omega_{12}^{2})}{(1 + a_{12}^{*})} \quad (12)$$

Note that χ_{12} and Y_{12} are considered zero, since the ethylene–vinyl acetate system constitutes a nonpolar–polar mixture (Huang and Stiel, 1987). The following combining rules for the molecular interaction parameters were used:

$$\epsilon_{12} = (\epsilon_1 \epsilon_2)^{1/2} \quad (13)$$

$$\rho_{o_{12}} = \frac{(\rho_{o_1} + \rho_{o_2})}{2} \quad (14)$$

$$a_{12} = \frac{a_1 + a_2}{2} \quad (15)$$

In Eqs. 13–15, the molecular parameters were obtained from the relationships given by Lin and Stiel (1977) for polar components and Tee et al. (1966) for nonpolar components. Using the combining rule given by Huang and Stiel for polar mixtures, the mixture critical properties for the ethylene–vinyl acetate nonpolar–polar system can be written as

$$\omega_m = x_1\omega_1 + x_2\omega_2 \quad (16)$$

$$Y_m = x_1 Y_1 + x_2 Y_2 \quad (17)$$

where Y_2 can be determined using Eq. 4. Also,

$$V_{cm}^{*} = \frac{[x_1^2 V_{c11}^{*} + 2x_1x_2V_{c12}^{*} + x_2^2 V_{c22}^{*}(1 + 0.17Y_2^{1.1})]}{[1 + 0.17Y_m^{1.1}]} \quad (18)$$

$$V_{cm}^{*}T_{cm}^{1.4} = x_1^2 V_{c11}^{*}T_{c11}^{1.4} + 2x_1x_2T_{c12}^{1.4}V_{c12}^{*} + x_2^2 V_{c22}^{*}T_{c22}^{1.4} \quad (19)$$

Note that the superscript, *, associated with the critical volume refers to the critical volume of a nonpolar fluid of equivalent size. Also, V_c (for pure components or interaction constants) is calculated from

$$V_{c12} = (0.2905 - 0.087\omega_{h12})R\frac{T_{c12}}{P_{c12}} \quad (20)$$

using an effective shape parameter, ω_{h12}, determined from

$$a_{12}^{*} = 0.1501 + 2.3724\omega_{h12} \quad (21)$$

The pseudocritical properties for the mixture were finally determined using Eqs. 16–21.

Results and Discussion

The objective of this work was to develop a method of predicting the thermodynamic properties of polar compounds (including mixtures) in general, and vinyl acetate systems in particular, at high pressures. After identifying the Wu and Stiel method for this purpose, it was decided to first try the Lee–Kesler method for nonpolar compounds at high pressures, since their method, which forms the basis of the Wu and Stiel method, is limited to $P_r = 10$ (Lee and Kesler, 1975). As a part of this process, Z, V, H and S were predicted for ethylene, nitrogen, propane and butane.

Figures 1 and 2 show comparison of the predicted properties of ethylene with IUPAC data (Jacobsen et al., 1988) at 13 randomly selected state points (as defined in Table 1) covering a range of pressures from 70 MPa to 240 MPa. Note that the temperature also varied over a range of 260 K to 320 K. The figures show a good agreement for all the three properties with maximum errors of 2.4%, 3.2% and 4.4% for V, ΔH and ΔS, respectively.

Table 1 lists the pressure, temperature, and composition corresponding to all the test points referenced in this article.

Table 2 shows comparisons with the data from Vargaftik (1975) for nitrogen, propane, and butane. One can see good agreement in the predicted properties, except in cases where the absolute values are small. These comparisons suggest that the Lee-Kesler equation of state can be applied at reduced pressures much higher than $P_r = 10$, at least for the compounds discussed above. This provided an impetus to attempt modification of the Wu and Stiel method for application to high pressures.

The next step was the application of the Wu and Stiel method to polar compounds at high pressures. Here again, as

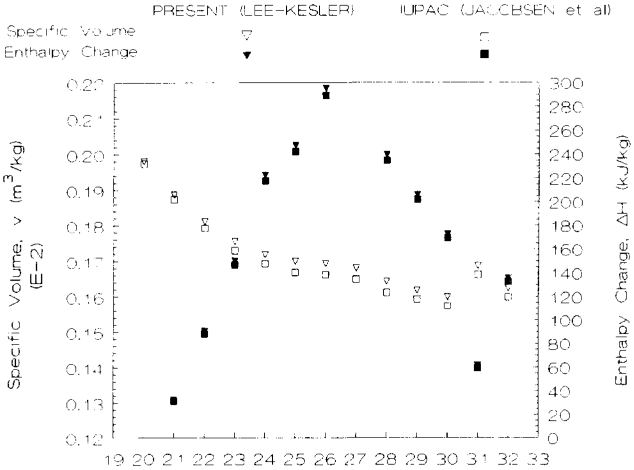

Figure 1. Comparison of specific volume and enthalpy change for ethylene.

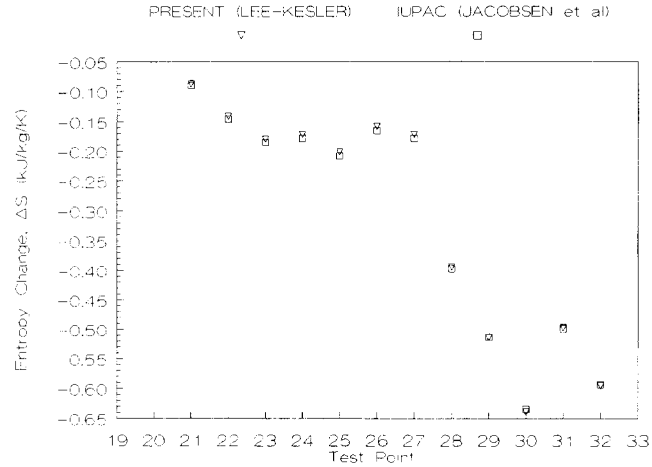

Figure 2. Comparison of entropy change for ethylene.

Table 1. Description of Test Points

Point No.	Pres. MPa	Temp. K	Composition of Ethylene/ Vinyl Acetate mol %	wt. %
1	20.68	300.00	96.506/3.494	90/10
2	68.93	288.89	96.506/3.494	90/10
3	103.39	311.11	96.506/3.494	90/10
4	172.32	344.44	96.506/3.494	90/10
5	241.25	366.67	96.506/3.494	90/10
6	275.72	311.11	96.506/3.494	90/10
7	310.18	422.22	96.506/3.494	90/10
8	20.68	311.11	87.75/12.25	70/30
9	68.93	300.00	87.75/12.25	70/30
10	103.39	311.11	87.75/12.25	70/30
11	172.32	344.44	87.75/12.25	70/30
12	241.25	366.67	87.75/12.25	70/30
13	275.72	311.11	87.75/12.25	70/30
14	19.30	311.11	75.425/24.575	50/50
15	103.39	311.11	75.425/24.575	50/50
16	103.39	377.78	75.425/24.575	50/50
17	206.79	366.67	75.425/24.575	50/50
18	227.47	366.67	75.425/24.575	50/50
19	241.25	366.67	75.425/24.575	50/50
20	70.00	290.33	100/0	100/0
21	100.00	290.33	100/0	100/0
22	140.00	295.33	100/0	100/0
23	180.00	300.33	100/0	100/0
24	220.00	310.33	100/0	100/0
25	240.00	310.33	100/0	100/0
26	260.00	320.33	100/0	100/0
27	270.00	320.33	100/0	100/0
28	270.00	290.33	100/0	100/0
29	270.00	275.33	100/0	100/0
30	270.00	260.33	100/0	100/0
31	180.00	260.33	100/0	100/0
32	240.00	260.33	100/0	100/0

a first step, the Wu and Stiel method was directly tried for predicting the properties of a mixture of ethylene and vinyl acetate. Three mixture compositions with 10, 30 and 50 wt. % of vinyl acetate were considered. The predictions were compared with experimental data from Monsanto Chemical Company. Disagreement as high as 8%–12% were observed for enthalpies and much higher values for entropies of the mixture. Errors of this magnitude are not acceptable for compressor performance prediction. Hence, it was decided to modify the Wu and Stiel method.

Equations of state in general are mainly empirical in nature involving a number of constants obtained by regression from experimental data. Like any of them, the Lee–Kesler's equation of state incorporates a large number of constants. Hence, initially, attempts were made to vary the constants in the Lee-Kesler equation of state for the simple and reference fluids. Subsequently, a simpler way of achieving the same end result was thought out, and instead of varying the constants in the Lee-Kesler equation of state, the compressibility factors for the simple and reference fluids were increased by using a multiplication factor, M_z. It was found that a value of 1.05 for M_z would make the experimental data agree quite well for all the three properties. M_z was found to have only a very weak dependence on composition with larger values needed with increasing concentration of the polar constituent. The constants for the Lee-Kesler equation of state given for simple and reference fluids were perhaps tailored to give good predictions only up to $P_r = 10$, and hence at higher pressures, predictions may not be accurate. This provided a justification for the introduction of M_z. However, it is interesting to note that M_z appears to depend on the constituents present in the mixture. This suggests that this simple constant alone might not be able to capture all the physics of molecular behavior and interaction occurring at high pressures and further work is necessary to understand the same.

Tables 3–5 show comparisons of the predicted V, ΔH, and ΔS for three compositions with the data from Monsanto and Quantum chemical companies. The data from Monsanto was experimentally obtained, while the Quantum data were analytically derived and subsequently validated using experimental data. The predictions show a very satisfactory agreement with both sets of data for all the three properties. Note that the state points for comparison were chosen randomly over a reasonably wide range of temperature and pressure for which the data were available and hence the agreement seen could be reasonably assumed to exist over the complete range. In particular, V and ΔH were predicted very well (with an average error in the range of 1%–2.5% for V and 1.5%–3% for ΔH), and even ΔS was predicted reasonably well. Note that Tables 3–5 and the range of errors discussed above were all obtained using a single value of 1.05 for the multiplication factor M_z. However, for the highest composition case, predictions were also done using $M_z = 1.07$ and a small improvement in the agreement with experimental data was noticed for Z and ΔH.

As mentioned in the Introduction, the only thermodynamic property data for vinyl acetate found in published literature were those of Kudchadker (1975) and Rätzsch and Findeisen (1980). Predictions of enthalpy and entropy from our method are compared with Kudchadker's data in Table 6. Keeping in mind that only a few data points were available in our range of interest, the agreement was reasonable in the lower temperature range and the disagreement increased at higher temperatures. Figure 3 compares the predicted (using $M_z = 0.98$) specific volume with the experimental data of Rätzsch and Findeisen over a wide range of pressure and tempera-

Table 2. Comparison of Predicted Properties from Lee-Kesler Method with Data of Vargaftik (1975)

Pres. MPa	Temp. K	Specific Volume m^3/kg Lee-Kesler	Specific Volume m^3/kg Vargaftik (1975)	Enthalpy Change kJ/kg Lee-Kesler	Enthalpy Change kJ/kg Vargaftik (1975)	Entropy Change kJ/kg/K Lee-Kesler	Entropy Change kJ/kg/K Vargaftik (1975)
				Propane			
20	280.33	0.001857	0.001799	0.0	0.0	0.0000	0.0000
20	370.33	0.002254	0.002223	232.9	232.3	0.7177	0.7151
30	370.33	0.002136	0.002102	236.8	236.1	0.6681	0.6707
41	370.33	0.002057	0.002021	243.8	242.6	0.6299	0.6304
61	310.33	0.001804	0.001761	112.0	114.7	0.1281	0.1433
61	370.33	0.001952	0.001917	262.3	260.3	0.5703	0.5727
				Nitrogen			
20	280.33	0.004308	0.004322	0.0	0.0	0.0000	0.0000
51	375.33	0.002972	0.002964	119.4	118.5	0.0421	0.0440
80	280.33	0.001848	0.001836	4.6	7.8	−0.5159	−0.5073
80	375.33	0.002274	0.002245	132.3	133.3	−0.1232	−0.1200
101	280.33	0.001690	0.001684	19.5	21.9	−0.5982	−0.5823
101	375.33	0.002020	0.002007	146.0	146.9	−0.2094	−0.1981
				Butane			
		Compressibility Factor Lee-Kesler	Compressibility Factor Vargaftik (1975)				
20	311.11	0.784	0.760				
41	344.44	1.427	1.390				
57	311.11	2.069	2.019				
57	344.44	1.944	1.894				
69	311.11	2.476	2.408				
69	344.44	2.320	2.263				

ture for which data are available. Very good agreement with errors less than 1%–2% was observed over the complete range. Note that a different value of M_z (equal to 0.98) was required for pure vinyl acetate. This would perhaps indicate that the constant is not just needed to account for the error in compressibility factor prediction at high pressures for the simple and reference fluids using the Lee–Kesler equation of state, but also perhaps the differences in the nature of interactions among different compounds.

This work has extended the Wu and Stiel method of predicting the thermodynamic properties to high pressures, for systems containing polar compounds in general and vinyl acetate in particular. Since the authors were interested mainly in vinyl acetate systems, which are commonly used in polyethylene production, the method was validated using the limited data available for the pure vinyl acetate and the ethylene–vinyl acetate system. Hence, further validation using data for other polar systems would help determine if this method is applicable to polar compounds in general.

Table 3. Comparison of Specific Volume of Vinyl Acetate and Ethylene Mixture

Comp. wt. %	Pres. MPa	Temp. K	Specific Vol. (m^3/kg) Present	Specific Vol. (m^3/kg) Monsanto	Specific Vol. (m^3/kg) Quantum
90/10	20.68	300.0	0.00232	0.00230	0.00229
90/10	68.93	288.9	0.00192	0.00189	0.00188
90/10	103.39	311.1	0.00187	0.00184	0.00184
90/10	172.32	344.4	0.00180	0.00176	0.00177
90/10	241.25	366.7	0.00174	0.00169	0.00171
90/10	275.72	311.1	0.00163	0.00157	0.00160
90/10	310.18	422.2	0.00174	0.00167	0.00169
70/30	20.68	311.1	0.00200	0.00206	0.00200
70/30	68.93	300.0	0.00172	0.00173	0.00171
70/30	103.39	311.1	0.00167	0.00167	0.00166
70/30	172.32	344.4	0.00162	0.00159	0.00160
70/30	241.25	366.7	0.00157	0.00154	0.00155
70/30	275.72	311.1	0.00147	0.00144	0.00146
50/50	19.30	311.1	0.00170	0.00177	0.00169
50/50	103.39	311.1	0.00147	0.00149	0.00147
50/50	103.39	377.8	0.00159	0.00161	0.00159
50/50	206.79	366.7	0.00143	0.00142	0.00142
50/50	227.47	366.7	0.00141	0.00141	
50/50	241.25	366.7	0.00141	0.00139	

Table 4. Comparison of Enthalpy Change for Vinyl Acetate and Ethylene Mixture

Comp. wt. %	Pres. MPa	Temp. K	Enthalpy Change (kJ/kg) Present	Enthalpy Change (kJ/kg) Monsanto	Enthalpy Change (kJ/kg) Quantum
90/10	68.93	288.9	8	−6	2
90/10	103.39	311.1	96	91	93
90/10	172.32	344.4	253	255	251
90/10	241.25	366.7	389	392	387
90/10	275.72	311.1	305	289	301
90/10	310.18	422.2	607	623	602
70/30	68.93	300.0	11	6	4
70/30	103.39	311.1	70	63	64
70/30	172.32	344.4	216	204	215
70/30	241.25	366.7	341	326	343
70/30	275.72	311.1	259	255	253
50/50	103.39	311.1	70	63	65
50/50	103.39	377.8	208	218	215
50/50	206.79	366.7	287	295	292
50/50	227.47	366.7	308	316	
50/50	241.25	366.7	322	331	328

Table 5. Comparison of Entropy Change for Vinyl Acetate and Ethylene Mixture

Comp. wt. %	Pres. MPa	Temp. K	Entropy Change (kJ/kg) Present	Monsanto	Quantum
90/10	68.93	288.9	−0.2929	−0.3540	−0.3226
90/10	103.39	311.1	−0.2128	−0.2464	−0.2346
90/10	172.32	344.4	−0.1144	−0.1253	−0.1299
90/10	241.25	366.7	−0.0691	−0.0716	−0.0880
90/10	275.72	311.1	−0.4839	−0.5451	−0.5112
90/10	310.18	422.2	0.1844	0.2195	0.1634
70/30	68.93	300.0	−0.2392	−0.2740	−0.2765
70/30	103.39	311.1	−0.2342	−0.2774	−0.2682
70/30	172.32	344.4	−0.1278	−0.1894	−0.1508
70/30	241.25	366.7	−0.0779	−0.1496	−0.0964
70/30	275.72	311.1	−0.4707	−0.5103	−0.4190
50/50	103.39	311.1	−0.1810	−0.2300	−0.2095
50/50	103.39	377.8	0.2187	0.2246	0.2263
50/50	206.79	366.7	0.0209	0.0122	0.0209
50/50	227.47	366.7	0.0008	−0.0096	
50/50	241.25	366.7	−0.0151	−0.0235	−0.0168

Table 6. Comparison of Enthalpy and Entropy Change for Vinyl Acetate with Kudchadker's (1975) Data

Pres. MPa	Temp. K	Enthalpy Change (kJ/kg) Present	Enthalpy Change (kJ/kg) Kudchadker (1975)	Entropy Change (kJ/kg/K) Present	Entropy Change (kJ/kg/K) Kudchadker (1975)
0.101	273.5	0.0	0.0	0.0000	0.0000
0.101	300.3	29.7	30.1	0.1035	0.1052
0.101	400.3	152.6	159.9	0.4559	0.4768
0.101	600.3	469.5	495.6	1.1040	1.1514

Conclusion

This work has provided a method of predicting the thermodynamic properties of vinyl acetate systems to pressures up to at least 400 MPa ($P_r = 80$). It has also provided the much needed property data for the ethylene–vinyl acetate system, which is lacking in public literature. Further, the method developed has potential for becoming a useful, universally applicable tool for general polar–nonpolar systems after further validation using other systems. During the course of this work, it was also established that the Lee-Kesler method could be applied to nonpolar compounds like ethylene, propane, butane and nitrogen at pressures much higher than those suggested in the literature. In the case of many compounds like ethylene, this would support the use of the Lee–Kesler method, instead of the more involved and computationally intensive techniques that are currently being used to predict thermodynamic properties at high pressures.

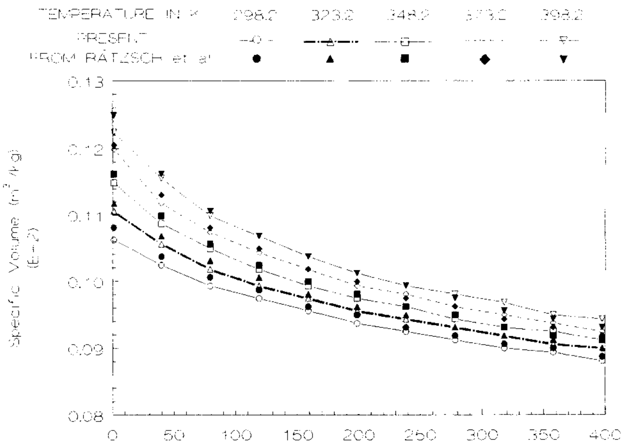

Figure 3. Comparison of predicted specific volume of vinyl acetate with experimental data of Rätzsch et al.

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Notation

a = radius of the spherical core, Å
$a^* = 2a/\rho_0$
H = enthalpy, kJ/kg
ΔH = enthalpy change, kJ/kg
ΔH^* = reduced enthalpy departure
P = pressure, MPa
R = gas constant, J/mol/K
S = entropy, kJ/kg/K
ΔS = entropy change, kJ/kg/K
T = temperature, K
V = specific volume, m^3/kg
x = mole fraction
Y = parameter for polarity effect correction used in Eq. 2
Z = compressibility factor

ϵ = energy parameter, J
κ = Boltzman constant
ρ = density, m^3/kg
ρ_0 = distance parameter
ω = acentric factor
χ = polarity factor as defined in Eq. 3

Subscripts

c = critical condition
cm = critical condition for the mixture
i,j = mixture component indices
ij = component interaction index
m = mixture
r = reduced values
ref = reference state
RS = reduced value at saturated condition
w = water
1,2 = parameters of components of a mixture
12 = interaction parameter

Superscripts

(r) = reference fluid function
(w) = water
0 = ideal gas state
(0) = simple fluid function
(1) = nonpolar fluid deviation function
(2) = polar fluid deviation function

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