T, T_c, T_R	temperature, critical temperature, or reduced temperature
v	volume
x	mole fraction of component in liquid phase
y	mole fraction of component in vapor phase
$\alpha(T_R,\omega)$	parameter used in determining equation of state constant
γ	liquid phase activity coefficient
δ_{ij}	parameter denoting i–j interaction
κ	parameter used in determining equation of state constant
ω	acentric factor

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Isothermal Vapor–Liquid Equilibria for the System 1,2-Dichloropropane–Propanal

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Vapor–liquid equilibrium data are determined for the system 1,2-dichloropropane–propanal at six temperatures. The system exhibits slight deviations from ideal behavior. The variation of g^E with composition suggests that the system may form an associated solution. The results are correlated with the Redlich–Kister and Wilson equations.

Binary systems containing propanal have not been studied intensively, and the literature is very poor on the subject (*1, 6, 8*). The main reason is the difficulty in obtaining accurate data for these systems because of the extreme instability of the aldehydes.

From a theoretical point of view, however, the equilibrium behavior of mixtures of polar molecules, such as the 1,2-dichloropropane–propanal system, is of interest; association between the aldehyde and the dichloropropane is expected. Furthermore, this system is very often applied in chemical processes (propylene oxide manufacture for instance).

Experimental Section

Purity of Material. The 1,2-dichloropropane purchased from Merck was employed without further purification, after gas chromatographic analysis failed to show any significant impurities. The propanal was an aqueous azeotrope, containing 1.8 wt % of water and having a normal boiling point of 47.87 °C. These values are somewhat different from those of Matsunaga and Katayama (*6*) (1.9 wt % and a normal boiling point of 47.8 °C). Before its use the aldehyde was distilled and dried over molecular sieves 3 Å in size (from Union Carbide). The physical properties of 1,2-dichloropropane and water-free propanal used for the measurement are summarized in Table I.

Apparatus and Procedure. The static isothermal ebulliometer is completely built of stainless steel (reservoir, valves, pipes). The complete description may be found in ref 3. Only slight modifications were made: the samples of the liquid phase for the analysis are withdrawn by applying vacuum and are immediately frozen in a liquid air trap. During the boiling the liquid phase is homogenized by a magnetic stirrer. The accuracy of the pressure measurements is better than 0.1 mmHg. The whole ebulliometer including the mercury manometer is maintained at a constant temperature (±0.02 °C) by a constant temperature bath. The temperature is measured by a Sneider thermometer with an accuracy of 0.02 °C. The analysis of the liquid phase is made with an Abbe refractometer. The calibration refractive index data appear in Table II. These data could be represented by three straight lines, with slopes, dn/dx, 0.0940 in the range of $0 \leqslant x_1 \leqslant 0.3$, 0.0766 in the range of $0.3 \leqslant x_1 \leqslant 0.6$, and 0.0630 in the range of $0.6 \leqslant x_1 \leqslant 1.0$. The accuracy of the composition within these ranges is equal to 0.002, 0.0026, and 0.0032, respectively. Because of the high volatility of the propanal, each refractive index determination was repeated several times and no appreciable deviation was observed in the measurements. Each composition was also confirmed by chromatographic analysis with a Perkin-Elmer 990 gas chromatograph.

Results

The total pressure measurements and the analysis of the liquid phase were made at six temperatures. The experimental results appear in Table III.

The vapor mole fraction and the liquid phase activity coefficients were calculated according to Barker's method (*2*). The fugacity coefficients in the vapor phase were obtained by using Löffler's equations (*5*) with three parameters (T/T_c, P/p_c, ω). For the binary vapor phase the mixing rule of Kay (*4*) was applied. The vapor pressures of the pure components are given by:

$$\log p_1^0 = 6.8271 - \frac{1216.60}{t + 212.57} \tag{1}$$

for 1,2-dichloropropane and

$$\log p_2^0 = 7.825\,98 - \frac{1595.57}{t + 274.63} \tag{2}$$

for propanal.

The Redlich–Kister and the Wilson equations were employed for the correlation of the activity coefficients.

The two-parameter Redlich–Kister equations are:

$$\ln \gamma_1 = (A + 3B)x_2^2 - 4Bx_2^3 \tag{3}$$

$$\ln \gamma_2 = (A - 3B)x_1^2 + 4Bx_1^3 \tag{4}$$

Table I. Physical Constants of Compounds

	1,2-Dichloropropane		Propanal	
	This work	Ref 9	This work	Ref 9
n_D^{20}	1.4384	1.4394	1.3620	1.3619
t_{nb}	95.71 °C	96.37	48.02 °C	48 °C
T_c	572.7 K	—	532.6 K	—
p_c	43.1 atm	—	67.8 atm	—
ω	0.256	—	0.167	—

Table II. Refractive Index of 1,2-Dichloropropane–Propanal Mixtures at 20 °C

x_1	n_D^{20}	x_1	n_D^{20}
0.0525	1.3675	0.4614	1.4031
0.0953	1.3720	0.4904	1.4061
0.1323	1.3758	0.5635	1.4106
0.1659	1.3783	0.6325	1.4151
0.2194	1.3828	0.6729	1.4218
0.2612	1.3880	0.7573	1.4239
0.3042	1.3918	0.8571	1.4298
0.3538	1.3950	0.8930	1.4319
0.4379	1.4020	0.9438	1.4348

The temperature dependent parameters A and B, obtained by minimization of the mean average deviation, σ, according to

$$\sigma^2 = \frac{1}{N}\sum_{i=1}^{i=N}\left[\frac{P_{\text{exptl}} - P_{\text{calcd}}}{P_{\text{exptl}}}\right]^2 \tag{5}$$

are shown in Table IV.

The temperature independent parameters of the Wilson equations,

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right] \tag{6}$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right] \tag{7}$$

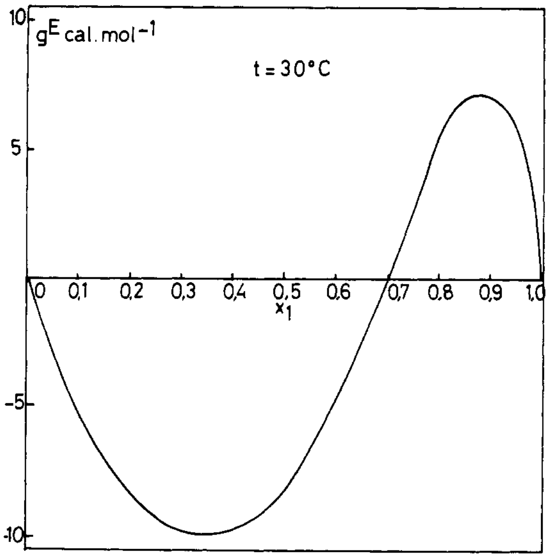

Figure 1. Excess Gibbs free energy of mixing against x_1 at 30 °C evaluated from the Wilson equations.

with

$$\Lambda_{12} = \frac{v_2}{v_1}\exp\left(-\left[\frac{\lambda_{12} - \lambda_{11}}{RT}\right]\right) \tag{8}$$

$$\Lambda_{21} = \frac{v_1}{v_2}\exp\left(-\left[\frac{\lambda_{12} - \lambda_{22}}{RT}\right]\right) \tag{9}$$

appear in Table IV, together with the values of the average deviation. The average deviations from the Redlich–Kister and Wilson equations are roughly of the same magnitude. Each correlation gives at each temperature activity coefficients with an extremum. The curve of the excess Gibbs energy (from Wilson as well from Redlich–Kister equations) against x_1 shows a peculiar form (Figure 1). The S-shaped curve is a real characteristic of this system and suggests the existence of strong interactions between the 1,2-dichloropropane and propanal molecules. The heat of mixing (not yet published experimental results) is exothermic and confirms the reality of the association within the solution.

Table III. Results of Vapor–Liquid Equilibrium Measurements (P in mmHg)

x_1	P(20 °C)	P(25 °C)	P(30 °C)	P(35 °C)	P(40 °C)	P(45 °C)
0.0909	236.90	292.01	356.84	433.59	523.14	627.83
0.203	211.52	261.82	321.28	391.07	472.38	566.60
0.275	194.64	240.02	292.91	354.02	424.06	503.73
0.320	183.19	227.07	279.05	340.13	411.42	494.06
0.471	149.58	185.06	228.21	278.21	336.46	403.85
0.603	121.72	151.21	186.43	228.23	275.52	335.27
0.657	113.15	139.96	172.16	210.65	256.42	310.60
0.732	92.62	116.59	145.12	178.75	218.05	263.60
0.862	71.85	90.28	112.53	139.17	170.86	208.32
0.937	55.87	50.84	92.00	115.47	143.05	175.11

Table IV. Parameters of Redlich–Kister and Wilson Equations

	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C
A	−0.004	−0.0100	−0.168	−0.022	−0.0301	−0.038
B	0.178	0.188	0.2079	0.221	0.238	0.246
σ_{R-K}, %	2	1.9	2	2.1	2.3	2.1
$(\lambda_{12} - \lambda_{11})/R$			−375 K			
$(\lambda_{12} - \lambda_{22})/R$			+655 K			
σ_W, %	2	2.1	2	1.47	1.54	1.76

Glossary

g^E	excess Gibbs energy
n_D	refractive index
P	total pressure
p^0	vapor pressure
R	gas constant
t, T	temperature in °C, K
T_c	critical temperature
v	molar volume cm^3 mol^{-1}

Greek letters

γ	activity coefficient
λ_{ij}	energy interaction
ω	acentric factor

Subscripts

1	1,2-dichloropropane
2	propanal

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Heat Capacities of Liquid Hydrocarbons. Estimation of Heat Capacities at Constant Pressure as a Temperature Function, Using Additivity Rules

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Additivity rules were applied to develop a scheme for estimating constant pressure heat capacity of liquid hydrocarbons as a temperature function. Values for 20 typical hydrocarbon groups and 12 structural features were derived from experimental data on 117 hydrocarbons. The various group values and the structural contributions, which are presented as cubic polynomial expressions, represent the most common groups in hydrocarbons. These group values can be used to estimate the heat capacity of almost any common liquid hydrocarbon below the boiling point. During this research, 1209 independent data points were examined; the standard deviation and the average deviation between the calculated and the observed values were found to be ±0.8 and ±0.64 cal mol^{-1} K^{-1}, respectively.

The need for data on heat capacities in designing a chemical plant is very obvious. Although experimental data can be very accurate, it is very difficult to provide all the data needed for every single compound. Moreover, in most cases, the accuracy required by the industry is less than ±1 cal mol^{-1} K^{-1}. For these reasons, several methods have been developed for estimating thermochemical properties and especially methods for estimating liquid heat capacities. Among these methods, it is worth mentioning the simple Kopp's rule (*4*), the Tsien method based on Lennard-Jones and Devonshire theory on normal liquids (*7*), and more recently methods developed by Yuan and Stiel (*8*), by Swenson and Chueh (*6*), and by Amirkhanov et al. (*1*). Although some of these methods are based on some theoretical consideration, they require much experimental input and relatively complicated calculations, their accuracy is marginal, and they are applicable only for a specific property (e.g., liquid heat capacity). A more detailed discussion of these methods, their range of applicability, their accuracy, and their relation to the work presented here is given in a recent manuscript (*9*).

An empirical approach for estimating thermochemical properties was established some 20 years ago by Benson and Buss (*2*), who developed a hierarchy of empirical additivity laws and demonstrated that thermochemical properties of gases, such as entropy, enthalpy, and heat capacity, could be estimated almost to the extent of the experimental uncertainty. Johnson and Huang (*10*), Missenard (*11*), and Shaw (*5*), have applied group methods to the estimation of liquid heat capacities.

Shaw demonstrated that $C_p(\mathrm{l})$ can be estimated to within ±1.0 cal mol^{-1} K^{-1} by group methods. The growing need for reliable and simple methods for estimating thermochemical data, mainly for the various energy research programs, has motivated us to extend this method so that heat capacities of liquids as a temperature function can be estimated easily, quickly, and accurately.

Data Sources

Heat capacity data as a temperature function are usually presented in the literature in intervals of 10 K. In this study, we

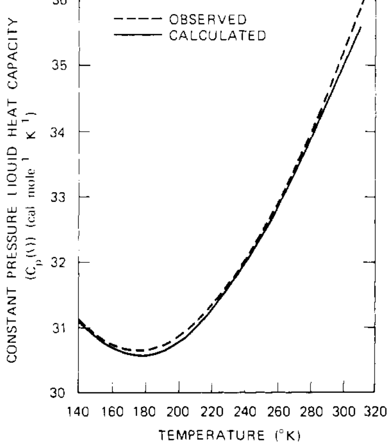

Figure 1. Schematic presentation of the agreement between observed calculated $C_p(\mathrm{l})$ for the case of 1-*cis*-3-pentadiene [$C_p(\mathrm{l}) = a + f + g + 2j + \alpha$].

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