Determination of Physicochemical Properties of Some Fatty Acid Methyl Esters by Gas Liquid Chromatography[1]

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Physicochemical data such as vapor pressures (p^0), heats of vaporization (ΔH_v), activity coefficients at infinite dilution (γ^∞) and excess partial molar entropy (ΔS_e^0) are considered important for conducting unit processes and designing reactor equipment. Scanty information regarding such data is available in the literature for the higher fatty acid methyl esters. The objective of this research was to determine the physicochemical properties of higher fatty acid methyl esters (C_{11}–C_{23}) by a gas-liquid chromatographic technique with SE-30 and diethylene glycol adipate as stationary phases. Correlations between carbon numbers and various thermodynamic properties have indicated definite trends, which could be useful in predicting the properties of unknown fatty acid methyl esters. The data generated may be useful to chemical engineers in the construction of storage tanks, solvent extractors and distillation columns.

KEY WORDS: Activity coefficient, DEGA, fatty acid methyl esters, gas liquid chromatography, heats of vaporization, physicochemical properties, SE-30, vapor pressure.

It is well established that thermodynamic data generated by gas-liquid chromatography (GLC) are fairly accurate and reliable (1). GLC has advantages over conventional techniques in the determination of physicochemical properties where sample purity is not essential. Small quantities of substances are sufficient for the experiments, and the method is quick. Moreover, thermodynamic data determined by GLC have been appearing in the literature frequently (2–6).

Methyl esters of fatty acids are useful intermediates in the preparation of alkanol amides, sucrose polyesters and alcohols (7–9). Further, they are proposed as fuel for diesel engines (9). Therefore, it is of practical importance to know the physicochemical properties of these compounds.

A thorough literature search revealed that few data are available (10–21) on the physicochemical properties of the methyl esters of the higher fatty acids, and prompted us to undertake the present investigations. In this paper, we describe the determination of physicochemical properties, such as vapor pressure, heat of vaporization (ΔH_v), activity coefficient (γ^∞) at infinite dilution, excess partial molar free energy of mixing (ΔG_e^0) at infinite dilution and excess partial molar entropy (ΔS_e^0), of twelve fatty acid methyl esters on two stationary phases.

EXPERIMENTAL PROCEDURES

Materials and methods. The fatty acids (capric, lauric, myristic, palmitic, stearic, oleic, linoleic, arachidic, behenic, elaidic, erucic and ricinoleic acids) were procured from Acme Synthetic Chemicals, Bombay, India, and stored in a cool place until analysis.

TABLE 1

Molecular Weights of GLC Stationary Phases Determined by Gel Permeation Chromatography and Vapor Pressure Osmometry[a]

Liquid phase	Molecular weight GPC	Molecular weight Osmometry	Average molecular weight
SE-30	11,900	12,100	12,000.0
DEGA	1,755.0	1.793.0	1,774.0

[a] Abbreviations: GLC, gas-liquid chromatography; GPC, gel permeation chromatography; DEGA, diethylene glycol adipate.

The stationary phases and supports used in gas chromatographic studies [*i.e.* SE-30 and diethylene glycol adipate (DEGA)] were purchased from Analabs (North Haven, CT). All the solvents used for the experiments were of either AR-grade or spectral-grade. Double-distilled water from an all-glass apparatus was used wherever necessary.

The molecular weights of the two stationary phases, *i.e.* SE-30 and DEGA, were determined by gel permeation chromatography (GPC) and vapor pressure osmometry. Results obtained are given in Table 1. Average values were used for the calculation of physicochemical properties of the fatty acid methyl esters.

Calculations were done on an EC-A Super 32/30 mainframe computer (ECIL, Hyderabad, India) with a Fortran - 4 program.

Preparation of methyl esters. Methyl esters were prepared by esterification of fatty acids with methanol containing 2% sulphuric acid. Purity was monitored by micro thin-layer chromatography (TLC). All the methyl esters prepared were >99% pure.

Gas-liquid chromatography. A Hewlett-Packard 5840 A gas chromatograph (Palo Alto, CA) with thermal conductivity detector and microprocessor was used for all the experiments. The following experimental conditions and columns were used.

Column 1: 10% DEGA on chromosorb W AW (80–100 mesh); injector and detector temperatures 300°C each; oven temperatures 180°C, 190°C, 200°C and 210°C. Column 2: 10% SE-30 on Chromosorb W AW 80–100 mesh); injector and detector temperatures: 300°C each; column temperatures: 240, 250, 260 and 270°C.

Hydrogen was used as carrier gas at a flow rate of 40 mL/min and the oven temperature was maintained with an accuracy of ± 0.3°C. The sample (0.2 μL) was injected and the retention time of each sample was noted. Retention volume of each sample was evaluated at four different temperatures by means of the equation (22):

$$V_g^o = \frac{P_o - P_w}{P_o} \times \frac{273}{T_a} \times F \times t_R \times \frac{1}{W_L} \times j \qquad [1]$$

where P_o = barometric pressure in cm Hg; P_w = pressure of water vapor in cm at room temperature; T_a = room temperature in °K; F = flow rate of the carrier gas at the

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outlet of the column; W_L = weight of the liquid phase in grams; t_R' = net retention time of the methyl ester; and j = gas compressibility factor, which is given by:

$$j = \frac{3}{2}\,\frac{\left(\frac{P_i}{P_o}\right)^2 - 1}{\left(\frac{P_i}{P_o}\right)^3 - 1} \qquad [2]$$

$P_i = P_o + P_x$ and P_x is the reading in cm Hg of a manometer arranged between the cylinder and the injection port.

All the other parameters are calculated from the V_g^0 value obtained from the above equation.

RESULTS AND DISCUSSION

Data obtained at various temperatures for ln V_g^0 are plotted against 1/T on SE-30 and DEGA stationary phases. The heats of vaporization (ΔH_v) data are obtained from the slopes of the graphs according to the procedure given elsewhere (1). Results are shown in Table 2, together with the reported data. There are large differences in the published data taken from three sources. However, we have taken average ΔH_v values from the reported data and compared them to our data. Error (%) and standard deviation are listed in Table 2. The reported values and the experimental values obtained are in reasonable agreement, which demonstrates the reliability of the experimental procedures. The error is slightly high for methyl caprate and methyl laurate.

Figure 1 shows the plot of carbon number and ΔH_v for saturated fatty acid methyl esters. It is evident that the curve is approximately linear. However, the ΔH_v of an unknown methyl ester could be predicted with reasonable accuracy by extrapolation. ΔH_v data for other compounds are found to be ragged, which may be due to the variation in the chemical structure.

Calculation of vapor pressures. The vapor pressures of the methyl esters are calculated from Clausius-Clapeyron equation:

$$\frac{d\ln p^0}{dT} = \frac{\Delta H_v}{RT^2} \qquad [3]$$

$$\ln p^0 = \frac{-\Delta H_v}{RT} + A \qquad [4]$$

By utilizing ΔH_v data from Table 2 and the vapor pressures reported at any one temperature, the vapor pressure for the esters at any required temperature can be calculated from equations [3] and [4]. The vapor pressure data thus calculated are given in Table 3.

The vapor pressures determined are in reasonable agreement with those calculated from Antoine constants taken from Boublik *et al.* (16) for the first six esters listed in Table 3. The deviations are slightly high for methyl caprate. However, for the determination of vapor pressures of esters of the higher fatty acids, the data given by Markley (11) were used.

Boiling points for the methyl esters at pressures of 0.1, 0.5 and 1.0 Torr are calculated from the experimental data and presented in Table 4.

Activity coefficients at infinite dilution and excess thermodynamic functions. Activity coefficients (γ^∞) are obtained from the expression (23):

$$\gamma^\infty = \frac{17.05 \times 10^6}{m\, p^0\, V_g^0} \qquad [5]$$

TABLE 2

Heats of Vaporization for the Methyl Esters Determined by Gas-Liquid Chromatography (GLC)

Ester	Reported (Cal/mole)[a,b] 1[c]	2[d]	3[e]	Average (Cal/mole)	Obtained by GLC (Cal/mole)	Error (%)	Standard deviation (σ)
Methyl caprate	—	15,810.0	13,831.7	14,820.5	11,922.0	19.56	296
Methyl laurate	—	14,659.0	14,853.5	14,756.3	12,744.0	13.64	215
Methyl myristate	17,550.0	16,335.0	16,051.0	16,645.3	15,612.0	6.21	152
Methyl palmitate	18,900.0	15,795.0	17,003.5	17,232.8	18,701.0	8.23	141
Methyl stearate	19,000.0	16,688.0	—	17,844.0	18,016.0	0.96	120
Methyl oleate	18,900.0	16,872.0	—	17,886.0	18,451.0	3.16	133
Methyl linoleate	18,750.0	—	—	—	18,451.0	1.59	108
Methyl arachidate	—	—	—	—	18,371.0	—	—
Methyl behenate	—	—	—	—	19,364.0	—	—
Methyl elaidate	—	—	—	—	18,441.0	—	—
Methyl erucate	—	—	—	—	22,343.0	—	—
Methyl ricinoleate	—	—	—	—	21,350.0	—	—

[a] To convert to joules per g mole, multiply the listed value by 4.184.
[b] To convert to K.Cal/mole, divide the listed value by 1000.
[c] Reported in ref. 11.
[d] Reported in ref. 12.
[e] Reported in ref. 21.

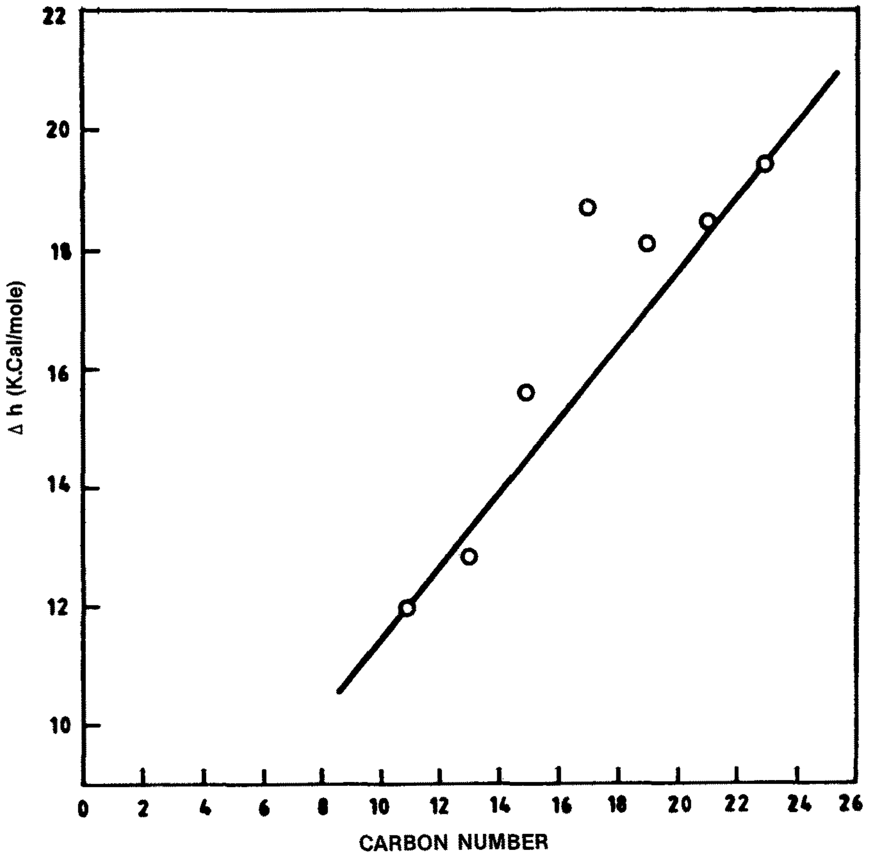

FIG. 1. Plot of ΔH_v, heats of vaporization against carbon number of the fatty acid methyl esters.

TABLE 3

Vapor Pressures in mm Hg for the Fatty Acid Methyl Esters at Various Temperatures

	Temperature (°K)							
Name of the ester	453	463	473	483	513	523	533	543
Methyl caprate	172.00[a]	229.50	301.90	392.50				
	180.00[b]	245.00	328.00	430.00				
Methyl laurate	67.30[a]	91.41	122.50	162.20				
	64.00[b]	90.00	125.00	170.20				
Methyl myristate	23.39[a]	34.02	48.70	68.70				
	23.00[b]	33.00	47.50	67.30				
Methyl palmitate	8.08[a]	12.65	19.45	29.40				
	8.23[b]	12.50	18.40	26.80				
Methyl stearate	—	—	—	—	33.28[a]	44.66	61.87	85.70
					34.00[b]	41.50	50.00	56.00
Methyl oleate	—	—	—	—	37.12[a]	52.50	73.20	100.90
					33.28[b]	44.66	61.87	84.70
Methyl linoleate	—	—	—	—	47.40	67.38	94.52	130.95
Methyl arachidate	—	—	—	—	18.56	26.19	36.49	50.23
Methyl behenate	—	—	—	—	10.01	14.40	20.42	28.60
Methyl elaidate	—	—	—	—	48.15	68.05	94.93	130.82
Methyl erucate	—	—	—	—	9.22	14.02	20.93	30.94
Methyl ricinoleate	—	—	—	—	18.84	28.12	41.34	59.92

[a] *Experimental results.*

[b] Calculated from Antoine constants taken from Boublik *et al.* (ref. 16).

TABLE 4

Boiling Points for the Methyl Esters at Various Pressures

	Boiling point (°K)		
Ester	0.1 Torr	0.5 Torr	1.0 Torr
Methyl caprate	285.26	308.90	320.33
Methyl laurate	310.27	336.48	349.17
Methyl myristate	344.61	370.79	383.32
Methyl palmitate	373.94	399.49	411.60
Methyl stearate	386.11	414.53	428.10
Methyl oleate	386.62	414.39	427.61
Methyl linoleate	383.12	410.37	423.34
Methyl arachidate	397.73	427.32	441.46
Methyl behenate	412.90	443.13	457.54
Methyl elaidate	382.43	409.59	422.52
Methyl erucate	425.29	452.86	465.87
Methyl ricinoleate	410.40	437.28	449.98

TABLE 5

Activity Coefficients and Excess Partial Molar Thermodynamic Quantities at Infinite Dilution on DEGA Stationary Phase[a]

Ester	Activity coefficients	Excess partial molar free energy of mixing at infinite dilution[b,c] (ΔGe^0)(Cal/mole)	Excess partial molar entropy (ΔSe^0 e.u.)
Methyl caprate	1.25	211.11	−2.60
Methyl laurate	1.62	452.02	−3.14
Methyl myristate	2.11	699.98	−2.00
Methyl palmitate	2.76	954.70	1.37

[a] Temperature, 473°K; DEGA, diethylene glycol adipate.

[b] To convert to joules per g mole, multiply the listed value by 4.184.

[c] To convert to K.Cal/mole, divide the listed value by 1000.

Excess partial molar free energies of mixing at infinite dilution ($\Delta G_e{}^0$) are calculated from the equation (23):

$$\Delta G_e{}^0 = RT \ln \gamma^\infty \qquad [6]$$

Molar heats of evaporation of solute from solution ($\Delta H_e{}^s$) are calculated from experimental $V_g{}^0$ values with the equation (24):

$$\Delta H_e^s = \log \frac{V_g\,(T_2)\,T_1}{V_g\,(T_1)\,T_2} \cdot \frac{2.303\ RT_2\ T_1}{T_1 - T_2} \qquad [7]$$

The excess partial molar enthalpies at infinite dilution ($\Delta H_e{}^0$) are obtained from

$$\Delta H_e{}^0 = \Delta H_v - \Delta H_e^s \qquad [8]$$

and following the evaluation of $\Delta G_e{}^0$ and $\Delta H_e{}^0$, excess partial molar entropies ($\Delta S_e{}^0$) are evaluated from (24):

$$\Delta G_e{}^0 = \Delta H_e{}^0 - T \cdot \Delta S_e{}^0 \qquad [9]$$

Values for γ^∞ of the methyl esters on DEGA and SE-30 stationary phases, together with excess partial thermodynamic quantities of methyl esters at 473°K and 513°K, are listed in Tables 5, 6 and 7, respectively.

An inspection of the activity coefficients given in these tables indicates that there are both negative and positive deviations from Raoults' law. Deviations are positive on the DEGA stationary phase and negative on the SE-30 stationary phase. Positive deviations on DEGA may be due to hydrogen bonding between the methyl esters and DEGA (also an ester). To get activity coefficients nearer to

TABLE 6

Activity Coefficients and Excess Partial Molar Thermodynamic Quantities at Infinite Dilution on SE-30 Stationary Phase[a]

Ester	Activity coefficient	Excess partial molar free energy of mixing at infinite dilution[b,c] ($\Delta G_e{}^0$) (Cal/mole)	Excess partial molar entropy ($\Delta S_e{}^0$ e.u.)
Methyl caprate	0.15	−1766.35	+2.77
Methyl laurate	0.16	−1715.49	+1.45
Methyl myristate	0.19	−1517.54	+1.83
Methyl palmitate	0.22	−1398.73	+5.27

[a] Temperature 473°K.

[b] To convert to joules per g mole, multiply the listed value by 4.184.

[c] To convert to K.Cal/mole, divide the listed value by 1000.

TABLE 7

Activity Coefficients and Excess Partial Molar Thermodynamic Quantities at Infinite Dilution on SE-30 Stationary Phase[a]

Ester	Activity coefficient	Excess partial molar free energy of mixing at infinite dilution[b,c] ($\Delta G_e{}^0$) (Cal/mole)	Excess partial molar entropy ($\Delta S_e{}^0$ e.u.)
Methyl stearate	0.28	−1300.617	+1.13
Methyl oleate	0.27	−1328.32	+2.66
Methyl linoleate	0.21	−1582.77	+1.86
Methyl arachidate	0.29	−1257.37	+0.95
Methyl behenate	0.26	−1381.13	+5.59
Methyl kelaidate	0.16	−1851.09	−4.51
Methyl erucate	0.28	−1297.33	+0.01
Methyl ricinoleate	0.27	−1348.10	−0.34

[a] Temperature 513°K.

[b] To convert to joules per g mole, multiply the listed value by 4.184.

[c] To convert to K.Cal/mole, divide the listed value by 1000.

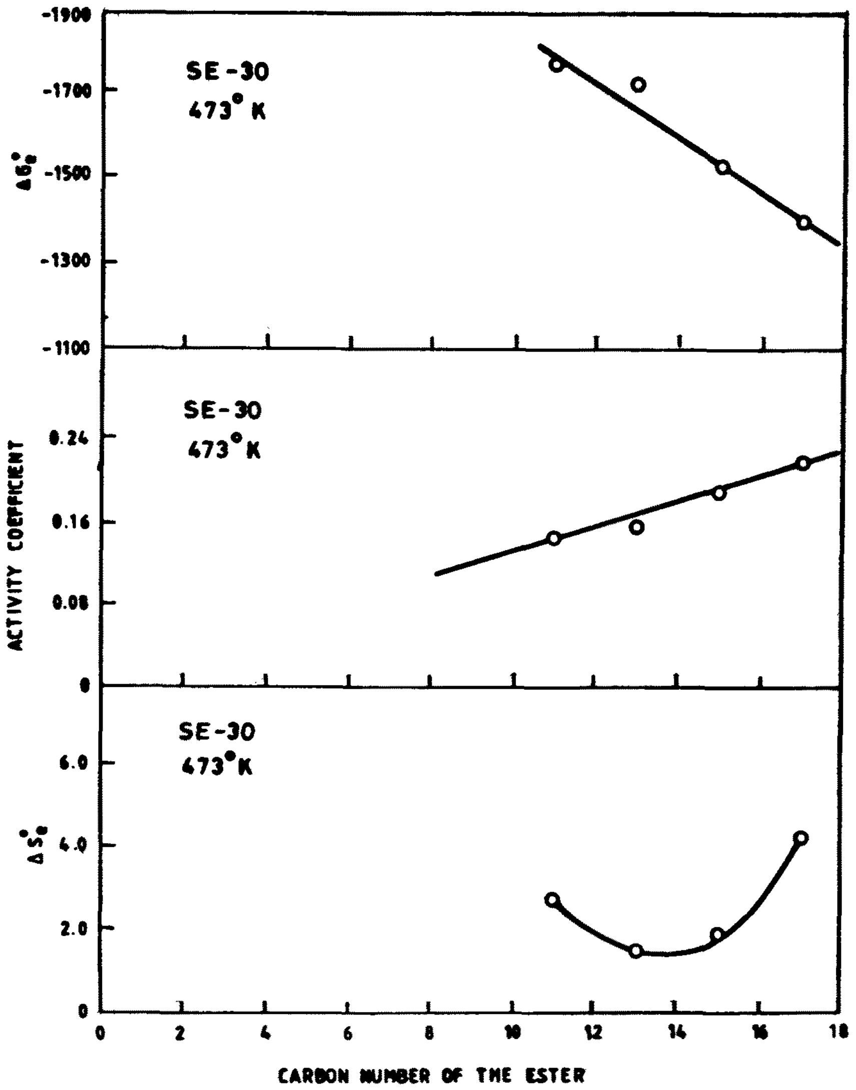

FIG. 2. Plots of $\Delta G_e{}^0$, activity coefficient and $\Delta S_e{}^0$ against carbon number of the methyl esters on SE-30 stationary phase.

1 or >1, equilibrium between the solute (injected substance) and solvent (stationary phase) should be well established. The negative deviations on the SE-30 stationary phase may be due to its large molecular weight. Only surface equilibrium is attained in the system between the ester and the stationary phase, whereas bulk equilibrium may not be attained. Values of γ^∞, $\Delta G_e{}^0$ and $\Delta S_e{}^0$ for four esters, *viz.*, methyl caprate, methyl laurate, methyl myristate and methyl palmitate, were generated at 473°K. For the remaining esters, the thermodynamic properties are shown at 513°K because of their higher boiling points.

It is evident from Tables 5, 6 and 7 that $\Delta S_e{}^0$ for all esters is small, indicating greater stability of the systems. Further, the positive entropy values indicate that the attainment of equilibrium in the chromatographic system is spontaneous.

Plots of carbon number of the methyl estes (C_{11}–C_{17}) *vs.* $\Delta G_e{}^0$, γ^∞ and $\Delta S_e{}^0$ on SE-30 and DEGA stationary phases are shown in Figures 2 and 3, respectively. These plots are drawn by using the thermodynamic data at 473°K. The correlations between the carbon number and γ^∞ and $\Delta G_e{}^0$ are found to be linear on both the stationary phases. These plots are helpful in predicting γ^∞ and $\Delta G_e{}^0$ of higher fatty acid methyl esters in DEGA and SE-30 stationary phases. Definite trends are not observed for $\Delta S_e{}^0$ on both stationary phases.

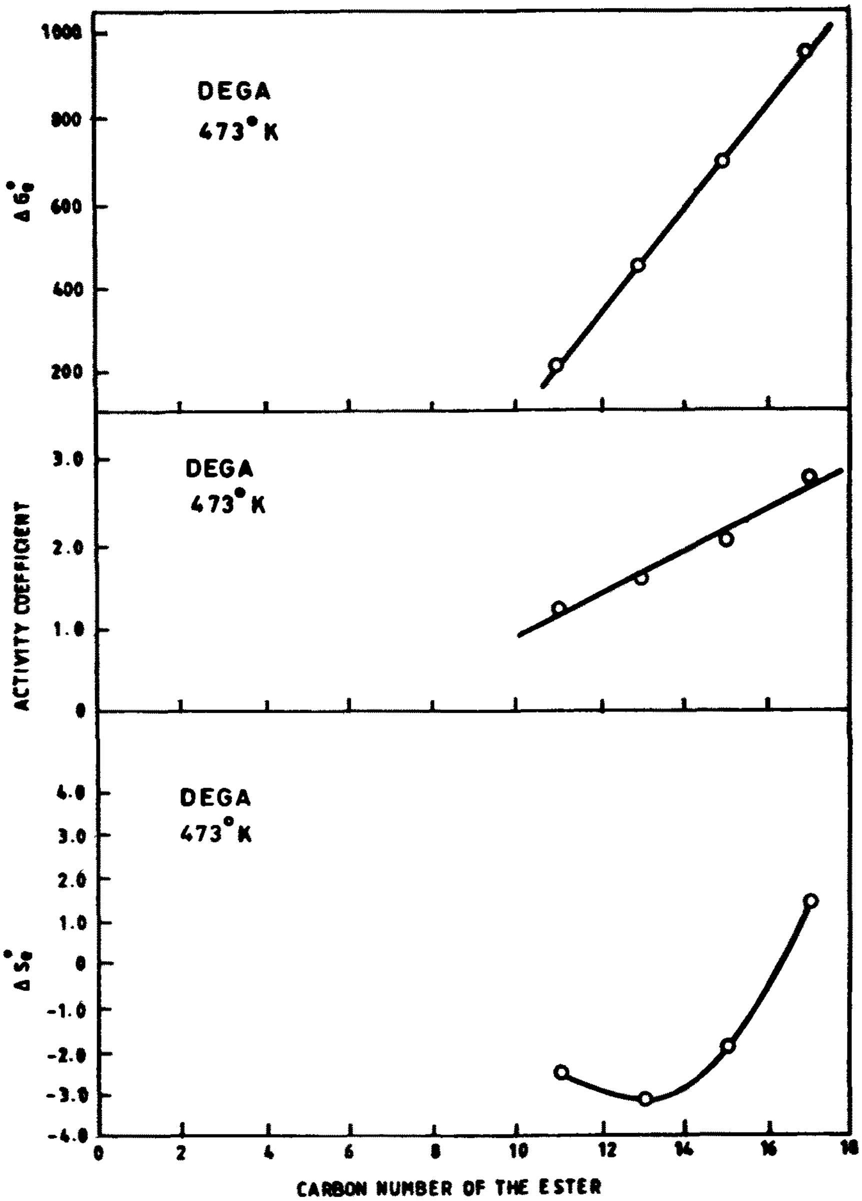

FIG. 3. Plots of ΔG_e^0, activity coefficient and ΔS_e^0, against carbon number of the methyl esters on diethylene glycol adipate (DEGA) stationary phase.l

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