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STANDARD MOLAR ENTHALPIES AND ENTROPIES OF VAPORIZATION FOR TWO LOW-MELTING TRICHLOROPHENOXY HERBICIDES

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The standard sublimation enthalpies of (2,4,5-trichlorophenoxy)acetonitrile and (2,4,5-trichlorophenoxy)aniline were determined by isothermal thermogravimetry using the Langmuir equation and by non-isothermal differential scanning calorimetry for comparison. The used procedure was previously tested using three reference compounds: benzoic acid, succinic acid and salicylic acid. The results compared to those reported in literature show an excellent agreement for two of the three compounds while the third agrees quite well. For (2,4,5-trichlorophenoxy)acetonitrile and (2,4,5-trichlorophenoxy)aniline, the extrapolation of data at 298.15 K were obtained, respectively: $\Delta_{\text{sub}}H°(298\text{ K})=\{(106\pm4)\text{ and }(101\pm4)\}\text{ kJ mol}^{-1}$. From Clausius Clapeyron equation obtained after the determination of the vaporization constant α', the following standard sublimation entropies for (2,4,5-trichlorophenoxy)acetonitrile and (2,4,5-trichlorophenoxy)aniline equal to $\Delta_{\text{sub}}S°(298\text{ K})=(251\text{ and }237)\text{ J K}^{-1}\text{ mol}^{-1}$, respectively, were derived, with an error of $\pm4\text{ J K}^{-1}\text{ mol}^{-1}$ equal for the studied herbicides.

Keywords: *isothermal thermogravimetry, Langmuir equation, phenoxy herbicides, standard vaporization enthalpy, vapor pressure*

Introduction

Chlorophenoxy derivatives are an important class of herbicides largely used in agriculture, industrial weed-control and forestry. These herbicides are commonly found in surface water and groundwater near agricultural fields [1]. Noticeable evidences indicate that volatilization from the soil surface may be an important pathway for loss of relatively persitent organochlorine pesticides [2]. Hence, temperature dependency of vapor pressure and vaporization enthalpy are crucial properties from which, together with other properties (i.e., soil adsorption and water solubility), it is possible to estimate the emission rates of herbicides from treated matrices (soil, foliage and water) [3].

Many authors used thermal analysis to study the thermal behaviour and stability of pesticides [4, 5] and to determine these parameters under different experimental conditions. Elder [6] measured the rate of sublimation of pharmaceutical compounds by thermal analysis, observing a linear relationship between vapor pressure and the rate of mass loss under isothermal condition. An Arrhenius temperature dependence of evaporation rate was found by Aggarwal *et al.* and the enthalpy of vaporization derived by the Clausius-Clapeyron equation was found to be close to the apparent activation energy [7]. Price and Hawkins introduced a procedure to estimate the vapor pressure of low-volatility substances by non-isothermal thermogravimetric measurements [8].

Conventional methods like that of vacuum-Knudsen effusion or that of torsion do not seem to be properly suitable for low-melting substances (whose melting temperature is below 373 K) due to the relatively low values of both experimental vapor pressures and temperatures. On the other hand, uncertainties associated to the enthalpy of vaporization obtained from non-isothermal differential scanning calorimetry (NI-DSC) can be sometimes quite high due to a doubtful evaluation of DSC baseline as well as of initial vaporization temperature.

By continuing our research program on the study of vaporization of chlorophenoxy herbicides [9], the aim of the present paper is to determine the standard sublimation enthalpies of (2,4,5-trichlorophenoxy)-acetonitrile (2,4,5-T Ac) and (2,4,5-trichlorophenoxy)-aniline (2,4,5-T An) from the rate of mass loss (dm/dt) measured by isothermal thermogravimetry (I-TG) at several given temperatures, T, through the Langmuir equation [10]:

$$p=[\mathrm{d}m/\mathrm{d}t(T/M)^{0.5}S^{-1}]\alpha'(2\pi R)^{-0.5}=Q\alpha'(2\pi R)^{-0.5} \quad (1)$$

where R is the gas constant, M is the molecular mass of the compound, α' is the vaporization constant, and S is the surface of the sample considered equal to the area of the bottom of the crucible. The corresponding vaporization enthalpies were derived considering the monomer, the only gaseous species present in the vapor phase of the studied compounds from the slope of

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the line obtained by plotting ln$Q$ *vs*. $1/T$, where Q=dm/dt(T/M)$^{0.5}S^{-1}$.

Before the above mentioned measurements were collected, in order to verify the reliability of the used procedure and to determine the value of α'(which is not unity in a flowing gas atmosphere [8]), calibration with reference compounds of known vaporization enthalpy and vapor pressures [11–14] was performed in the same temperature range of the examined herbicides using the same experimental conditions. The three reference compounds considered in the present work are: benzoic acid (BEA), succinic acid (SUA) and salicylic acid (SAA).

Experimental

BEA and SUA were supplied by Merck, SAA was provided by Fluka, while 2,4,5-T Ac and 2,4,5-T An by Sigma-Aldrich. Purity of all tested substances is over 99%, as certified by the suppliers; therefore, they were used as received without further purification.

The I-TG as well as the NI-DSC measurements were carried out on a Stanton-Redcroft 625 simultaneous TG/DSC connected to a 386 IBM-compatible personal computer. Instrument calibration was performed by using several very pure standards (indium [9], tin [9], and benzoic acid [12, 13]) having well known temperature and melting enthalpy.

I-TG measurements were carried out after heating the sample at 8 K min^{-1} up to the selected temperature and recording mass loss and sample temperature as a function of time. Rising temperature experiments were carried out on the sample and the experimental data were collected at every 1 K to give accuracy to the results. For each compound almost three vaporization runs were carried out under a stream of argon in the temperature range from ambient to 620 K at 5 K min^{-1} and the

Table 1 Langmuir parameters related to sublimation of benzoic acid under isothermal conditions

	T±0.2/K	$\Delta m/S$±0.0002/kg m^{-2}	Δt±5/s	–ln$Q$/kg K$^{1/2}$ s^{-1} m^{-2}
Run 1	342.6	0.000	140	12.6±5.8
	341.9	0.000	160	13.4±11.0
	341.7	0.000	140	12.9±7.8
Run 2	350.8	0.001	200	12.0±2.3
	350.6	0.001	200	12.1±2.5
	350.7	0.001	180	12.0±2.5
Run 3	356.3	0.001	164	11.5±1.6
	355.3	0.001	224	11.7±1.4
	355.6	0.001	121	11.3±1.8
Run 4	361.5	0.001	180	11.1±1.1
	360.3	0.001	160	11.2±1.3
	360.2	0.001	121	11.3±1.9
Run 5	366.8	0.002	142	10.7±0.9
	366.1	0.002	180	10.8±0.8
	365.7	0.002	160	10.8±0.9
Run 6	371.6	0.002	140	10.3±0.7
	370.6	0.003	160	10.4±0.6
	370.6	0.002	148	10.4±0.7
Run 7	376.9	0.003	121	10.0±0.5
	376.2	0.003	121	10.0±0.5
	376.3	0.003	140	10.0±0.5
Run 8	381.3	0.005	140	9.6±0.3
	380.6	0.005	140	9.6±0.3
	380.6	0.005	141	9.7±0.4
Run 9	389.7	0.008	106	8.9±0.2
	388.9	0.008	120	9.0±0.2
	388.5	0.008	135	9.0±0.2

Table 2 Langmuir parameters related to vaporization of benzoic acid under isothermal conditions

	T±0.2/K	$\Delta m/S$±0.0002/kg m^{-2}	Δt±5/s	–ln$Q$/kg K$^{1/2}$ s^{-1} m^{-2}
Run 1	415.0	0.025	81	7.4±0.1
	416.4	0.053	160	7.3±0.1
	414.4	0.046	160	7.5±0.1
Run 2	419.8	0.031	81	7.2±0.1
	419.0	0.025	73	7.3±0.1
	419.7	0.030	88	7.3±0.1
Run 3	420.8	0.041	101	7.1±0.1
	423.7	0.047	101	7.0±0.1
	422.8	0.044	101	7.1±0.1
Run 4	422.9	0.037	82	7.0±0.1
	423.4	0.038	81	7.0±0.1
	422.3	0.031	71	7.1±0.1
	420.8	0.048	121	7.1±0.1
Run 5	430.6	0.060	101	6.7±0.1
	431.3	0.085	140	6.7±0.1
	430.9	0.069	121	6.8±0.1
	430.4	0.137	241	6.77±0.03
Run 6	440.6	0.084	82	6.2±0.1
	442.2	0.131	120	6.1±0.1
	441.3	0.102	101	6.2±0.1
Run 7	445.4	0.054	50	6.1±0.1
	447.4	0.057	49	6.0±0.1
	448.6	0.047	40	6.0±0.2
Run 8	453.3	0.094	61	5.8±0.1
	455.3	0.082	49	5.7±0.1
	455.8	0.077	46	5.7±0.1
Run 9	455.8	0.077	46	5.7±0.1
	459.1	0.045	24	5.5±0.2
	460.6	0.043	22	5.5±0.3

uncertainty in the temperature measurements was found to be ±0.5 K. For all measurements an open aluminium crucible, with a cross sectional area of $2.0\cdot10^{-5}$ m^2, was used to contain the sample while an empty one of equivalent mass was used as reference. All the examined samples were placed in an argon-filled dry box in the crucible. The surface area of the molten compounds was considered equal to the area of crucible bottom and practically constant during the vaporization of the samples. The simultaneous TG/DSC system was flushed with pure gas stream both below (flow rate 50 mL min^{-1}) and above (flow rate 80 mL min^{-1}) the open pans, in order to remove the vapor during the vaporization of the sample. Because of the sensitivity of the used equipment, the vaporization kinetics could not be performed for mass loss rate below $5\cdot10^{-5}$ kg s^{-1}, so that all the vaporization measurements were carried out above the molten compounds at temperatures where the rate of mass loss was detectable. Sample size of about 7–10 and 4–6 mg of the studied compound were used for the I-TG and NI-DSC experiments, respectively.

Results and discussion

In order to obtain the rate of mass loss under isothermal condition from I-TG measurements the mass loss and temperature dependencies on time of BEA are given in Fig. 1, as an example. Q values of Eq. (1) are calculated from the difference Δm between two adiacent experimental mass values (represented by open circles in the linear portion of the I-TG curve,

Table 3 Temperature dependence of Q, sublimation and vaporization enthalpies of reference compounds

Compound	Process	No. of points	ΔT/K	$\ln Q^{a}$/kg K$^{1/2}$ m^{-2} s^{-1}		$\Delta H(T)$/kJ mol^{-1}	
				A^{d}	B^{d}	This work	Ref.
Benzoic acid	sub^{b}	9	342–389	19.04±0.73	10909±265	92±2	89 [12]
	vap^{c}	9	422–458	11.99±0.45	8056±195	67±2	68 [13]
Succinic acid	sub^{b}	7	418–455	26.42±0.85	15879±373	132±3	123 [14]
	vap^{c}	8	471–501	17.59±1.93	11451±942	98±8	94 [15]
Salicylic acid	sub^{b}	9	383–422	19.18±0.60	11311±242	94±2	95 [13]
	vap^{c}	9	441–470	13.98±0.54	9242±244	77±2	79 [13]

$^{a}\ln Q=A-B/T$(K); ^{b}sub=sublimation; ^{c}vap=vaporization; ^{d}the quoted errors are standard deviations

Table 4 Q Langmuir parameters related to vaporization of 2,4,5-TAc under isothermal conditions

	T±0.2/K	$\Delta m/S$±0.002/kg m^{-2}	Δt±5/s	$-\ln Q$/kg K$^{1/2}$ s^{-1} m^{-2}
Run 1	405.7	0.005	239	10.4±0.3
	405.0	0.003	140	10.5±0.5
	406.0	0.004	161	10.4±0.4
Run 2	416.5	0.007	160	9.8±0.3
	415.4	0.007	181	9.9±0.2
	416.4	0.004	101	9.7±0.4
Run 3	419.3	0.005	121	9.9±0.4
	421.9	0.008	140	9.5±0.2
	420.1	0.006	121	9.6±0.3
	418.1	0.007	140	9.6±0.3
Run 4	434.6	0.014	141	8.9±0.1
	434.2	0.012	116	8.9±0.2
	434.8	0.010	103	8.9±0.2
Run 5	438.8	0.016	121	8.6±0.1
	439.9	0.016	121	8.6±0.1
	438.6	0.015	121	8.7±0.1
	437.3	0.016	140	8.8±0.1
Run 6	457.0	0.024	91	7.9±0.1
	456.7	0.027	106	7.9±0.1
Run 7	462.4	0.037	106	7.6±0.1
	461.1	0.035	104	7.7±0.1
Run 8	462.8	0.043	135	7.7±0.1
	467.5	0.054	150	7.6±0.1
Run 9	471.6	0.040	81	7.3±0.1
	470.4	0.037	81	7.3±0.1
	469.9	0.030	68	7.4±0.1
Run 10	492.6	0.278	244	6.4±0.0
	492.8	0.066	67	6.6±0.1
	491.8	0.051	67	6.8±0.1
Run 11	498.9	0.083	61	6.2±0.1
	502.7	0.077	54	6.2±0.1
	504.3	0.057	41	6.2±0.1

Table 5 *Q* Langmuir parameters related to vaporization of 2,4,5-TAn under isothermal conditions

	T±0.2/K	$\Delta m/S$±0.002/kg $\mathrm{m^{-2}}$	Δt±5/s	$-\ln Q$/kg $\mathrm{K^{1/2}\ s^{-1}\ m^{-2}}$
Run 1	462.5	0.008	101	9.1±0.2
	463.3	0.008	101	9.1±0.2
	461.5	0.009	121	9.2±0.2
Run 2	473.7	0.052	379	8.6±0.0
	473.7	0.014	121	8.7±0.1
	472.9	0.014	121	8.7±0.1
Run 3	481.8	0.025	140	8.3±0.1
	484.1	0.028	140	8.2±0.1
	482.3	0.019	101	8.2±0.1
Run 4	491.2	0.063	239	7.9±0.0
	491.0	0.024	101	8.0±0.1
	489.4	0.018	81	8.1±0.1
Run 5	499.3	0.061	200	7.7±0.0
	499.4	0.024	81	7.8±0.1
	498.9	0.026	81	7.7±0.1
Run 6	504.0	0.134	319	7.4±0.0
	504.4	0.045	121	7.5±0.1
	503.2	0.036	101	7.6±0.1
Run 7	513.5	0.099	160	7.0±0.0
	512.9	0.047	81	7.1±0.1
	511.3	0.055	101	7.2±0.1
Run 8	520.6	0.028	41	6.9±0.2
	523.3	0.030	41	6.8±0.2
	525.5	0.027	41	7.0±0.2
Run 9	528.8	0.077	81	6.6±0.1
	530.8	0.076	81	6.6±0.1
	530.5	0.050	62	6.7±0.1
Run 10	539.0	0.045	35	6.3±0.2
	540.1	0.038	29	6.3±0.2
	540.6	0.041	36	6.4±0.2

Fig. 1), lost in a given time interval at fixed constant temperatures, divided by *S*. The obtained results are summarized in Tables 1 and 2 for sublimation and vaporization of BEA, respectively. An identical procedure was applied for SUA and SAA even if the results were not shown in the paper. The plot of the logarithm of the average *Q* values *vs.* $1/T$ is given in Fig. 2 for each run at constant temperature for the reference compounds. From the slopes of the corresponding lines obtained by the least squares method the $\Delta_{\mathrm{vap}}H(T)$ values were derived at the middle experimental temperature. These results as well as slopes and intercepts of the regression equations are reported in Table 3 with their standard deviations. Comparison

Table 6 Temperature dependence of *Q* and vaporization enthalpies of the studied compounds

Compound	No. of points	ΔT/K	$\ln Q^{a}$/kg $\mathrm{K^{1/2}\ m^{-2}\ s^{-1}}$		$\Delta H(T)$/kJ $\mathrm{mol^{-1}}$	
			A^{b}	B^{b}	this work	from NI–DSC
2,4,5,-T Ac	9	420–502	11.54±0.40	8898±114	74±1	73±4
2,4,5,-T An	8	462–540	16.37±1.7	9091±199	76±2	75±4

[a]$\ln Q=A-B/T(\mathrm{K})$; [b]the quoted errors are standard deviations

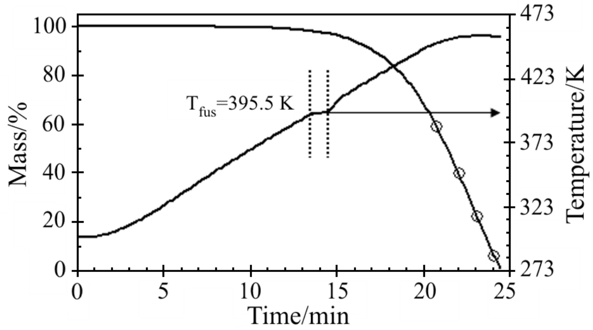

Fig. 1 I-TG curves of BEA at about 455 K. Experimental mass data (○) were used to determine the Q values

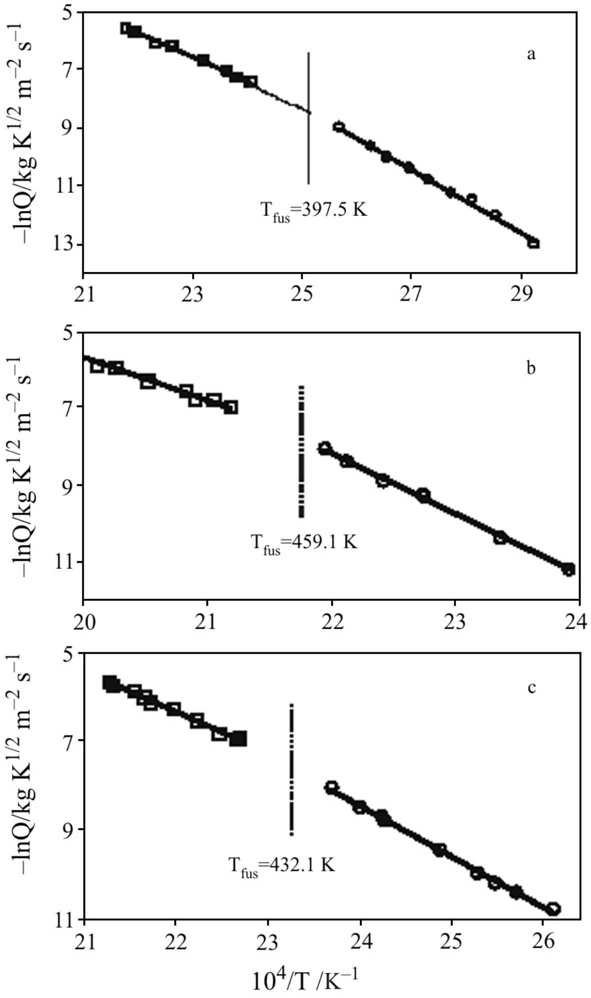

Fig. 2 Isothermal temperature dependencies of Q values for sublimation (□) and vaporization (○) of a – BEA; b – SUA and c – SAA

of these data with those found in literature [14–17] shows a good agreement among them, thus confirming that the reliability of the used procedure is good.

Therefore, from the I-TG data recorded at several selected temperature the corresponding Q values for 2,4,5-T Ac and 2,4,5-T An were derived and given

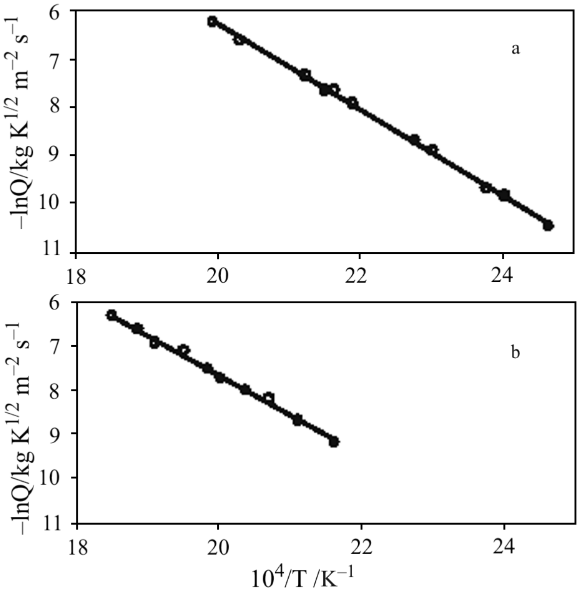

Fig. 3 Isothermal temperature dependencies of Q values for vaporization of: a – 2,4,5-T Ac and b – 2,4,5-T An

in Tables 4 and 5, respectively. The temperature dependencies of Q values for the two studied herbicides are represented by the plots of ln$Q$ *vs.* $1/T$ reported in Fig. 3. The $\Delta_{vap}H(T)$ values at the average temperature, obtained from the slopes of the corresponding regression lines for 2,4,5-T Ac and 2,4,5-T An (74±1 and 76±2 kJ mol^{-1}, respectively), were given in Table 6 together with those calculated from NI-DSC for comparison purposes as no enthalpy values were found in literature for these substances. An excellent agreement was found among the mentioned values.

These enthalpies were extrapoled at 298 K by using the difference in the heat capacity of vapor and solid as well as that of vapor and liquid as suggested by Chickos *et al.* [18]: $\Delta c_p(v,s)$=32 J K mol^{-1} and Δc_p(v,l)=54 J K mol^{-1}. To this purpose, the corresponding molar heats of fusion for 2,4,5-T Ac and 2,4,5-T An were considered. The obtained results, determined from melting NI-DSC peaks (Fig. 4), were found to be 26±1 and 16±1 kJ mol^{-1}, respectively. The calculated $\Delta_{sub}H°(298)$ values for 2,4,5-T Ac and 2,4,5-T An were found to be 106±2 and 101±3 kJ mol^{-1}, respectively. The associated uncertainties were considered as the sum of those estimated for $\Delta_{vap}H(T)$ and $\Delta_{fus}H$.

In order to obtain the temperature dependencies of vapor pressure for the studied compounds, the vaporization constant α' was determined from the slope of the $p(2\pi R)^{0.5}$ *vs.* Q plot of the reference compounds BEA, SUA and SAA, where their vapor pressures are taken from literature [19] for the experimental temperature range were their vaporization occur. The $p(2\pi R)^{0.5}=f(Q)$ plot for BEA is given in Fig. 5 as an

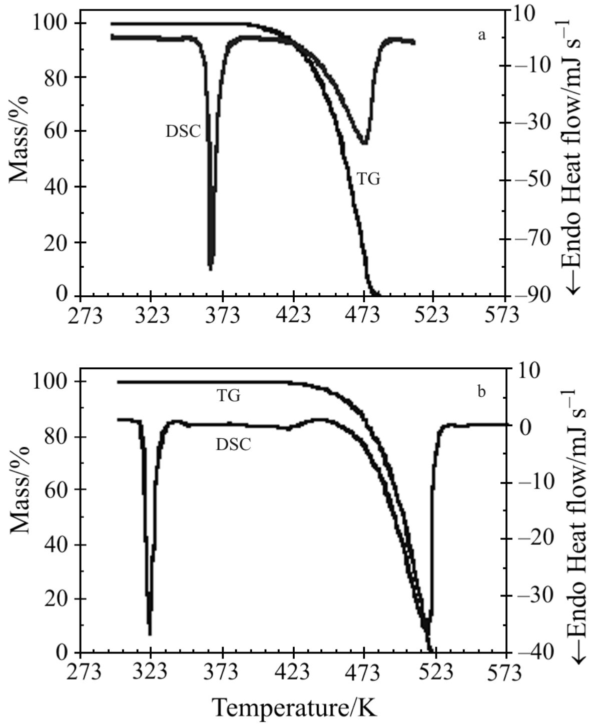

Fig. 4 NI-TG and DSC curves carried out at 5 K min^{-1} under a stream of argon for: a – 2,4,5-T Ac and b – 2,4,5-T An

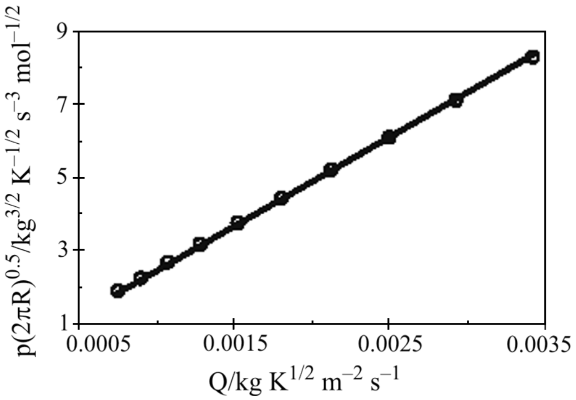

Fig. 5 $p(2\pi R)^{0.5}$ *vs.* Q plot for BEA

example. Therefore, weighting the slopes of the $p(2\pi R)^{0.5}$ *vs.* Q plots the following regression equations for BEA, SUA and SAA were respectively obtained:

$$p(2\pi R)^{0.5} = (2438\pm8)\cdot Q \tag{2}$$

$$p(2\pi R)^{0.5} = (2429\pm10)\cdot Q \tag{3}$$

$$p(2\pi R)^{0.5} = (2443\pm9)\cdot Q \tag{4}$$

The uncertainties associated to the obtained slopes are standard deviations. As no significant difference were found among the slopes of Eqs (2–4) a mean value of the vaporization constant α'= 2437±8 kg s^{-1} m^{-2} K^{-1} was derived in the range 422–501 K. Once α' has been determined it was used to derive the temperature dependence of vapor pressure from the corresponding Q values at the same temperatures. The obtained results in the form of Clausius-Clapeyron plots were given in Fig. 6. From the absolute vapor pressures the sublimation entropies of 2,4,5-T Ac and 2,4,5-T An, $\Delta_{\text{sub}}S°(T)\approx\Delta_{\text{sub}}S°(298)$=(251 and 237) J mol^{-1} K^{-1}, respectively, were determined with estimated errors of ±4 J mol^{-1} K^{-1} for both compounds.

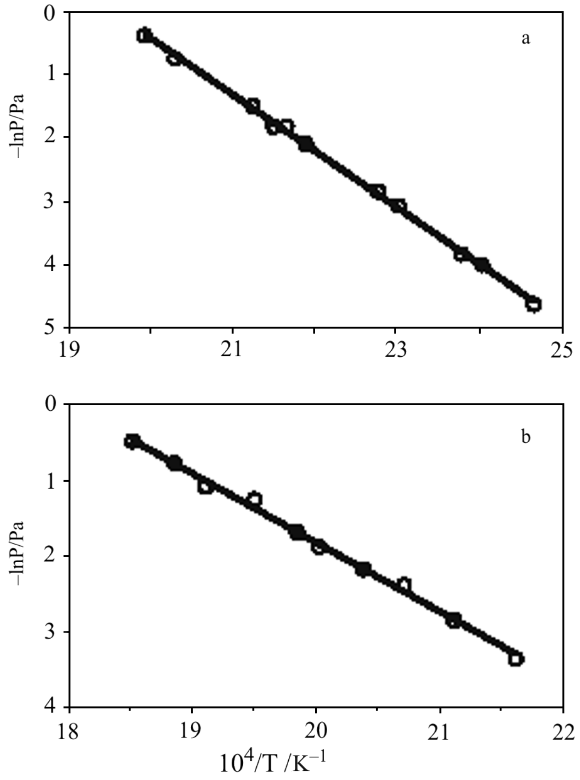

Fig. 6 Clausius-Clapeyron plot of: a – 2,4,5-T Ac and b – 2,4,5-T An

Conclusions

Isothermal TG measurements were used to obtain standard molar enthalpies and entropies of two low-melting phenoxyherbicides (2,4,5-TAc and 2,4,5-TAn) using the Langmuir equation. The proposed method was previously tested using benzoic, succinic and salicylic acids as reference compounds. Comparison with vaporization enthalpy values taken from literature show excellent agreement for benzoic acid and quite good agreement for succinic and salicylic acids. Further comparisons were made with values derived from non-isothermal DSC measurements and the results agree very well. Molar entropies extrapoled at 298.15 K are quite close to those of some dichlorophenoxy herbicides previously studied by the author of the present paper.

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