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The initial thermal characterization of hair color rinse ingredients — adipic acid

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Abstract

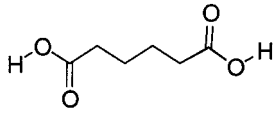
In this preliminary examination of various ingredients used in hair color rinses, thermal analysis studies were concluded for adipic acid. The instrument used was a simultaneous TG–DTA unit. The sample was subjected to thermal treatment in a nitrogen atmosphere at various heating and flow rates. At the very least, the data collected was used in ''finger printing'' the material, so that its presence in a formulation might be detected by this method. However, it has proved to be possible to offer a more detailed description than just fingerprinting and identification. By using the TG plot, the rate of evaporation for adipic acid was calculated and shown to agree with models for evaporation.

Keywords: Evaporation; Thermogravimetry; Adipic acid; Hair color rinses

1. Introduction

Adipic acid is a buffering and neutralizing agent that has been used in hair color rinses as well as plasticizers and nylon production. Hair rinses are aqueous-alcoholic solutions combined with azo dyes that coat the cuticle layer of the hair shaft with a temporary color without altering the natural pigments in the cortex layer. The base is usually tartaric acid (adipic acid, citric acid, acetic acid, and other acids have also been used) with which water-soluble azo dyes are blended [1]. The rinse is applied after shampooing the hair and is not rinsed out. The dye usually disappears in the next shampooing. When water has evaporated, a deposit is left behind, which forms a film [2]. For this reason, the study of the evaporation process of hair color rinse ingredients is very important in determining the effectiveness of the product to deposit dye onto the hair surface.

Adipic acid is also known as hexanedioic acid or 1,4-butanedicarboxylic acid. The empirical formula is $C_6H_{10}O_4$ with a molecular weight of 146.14. Its structural formula can be represented as:



Adipic acid is characterized as a colorless, needlelike substance that is insoluble in water. According to the literature, the melting and boiling points are 152 and 337.5°C at 1 atm, respectively [3].

Thermogravimetry has proven to be a very efficient method of studying the evaporation of cosmetics [4]. During a rising temperature program, the mass loss of a substance from a constant surface area in a

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controlled atmosphere can be recorded using a simultaneous TG–DTA unit. The data collected will produce a TG curve of mass loss against temperature or time. The derivative of percentage mass loss with respect to time can also be measured and plotted against temperature producing a DTG curve. The vapor pressure curve can be used to formulate the Antoine constants and such constants are available for adipic acid. The Antoine constants can then be used to test the model for evaporation inherent in the Langmuir equation, which has been employed by Price and Hawkins [5] using DTG data for various substances.

As a result, the vapor pressure curve of adipic acid can be resolved with the help of the Langmuir equation and checked using the Antoine equation. For evaporation studies, the form of the Langmuir equation used is as follows:

$$\frac{\mathrm{d}m}{\mathrm{d}t\,a} = p\alpha\left(\frac{M}{2\pi RT}\right)^{1/2} \tag{1}$$

where the rate of mass loss per unit area ($\mathrm{d}m/\mathrm{d}t\ a$) is in units of kg s^{-1} m^{-1}, the vapor pressure (p) is in units of Pa, the vaporization constant (α) has no units, the molecular weight of the evaporating species (M) is in units of kg mol^{-1}, the gas constant (R) is in units of J K^{-1} mol^{-1}, and the absolute temperature (T) is in units of K. Eq. (1) can be converted into a form better suited for the analysis of the TG data.

$$p = kv \tag{2}$$

In Eq. (2), k is substituted for $\alpha^{-1}(2\pi R)^{1/2}$, and v is $(T/M)^{1/2}(\mathrm{d}m/\mathrm{d}t\ a)$. To determine the effect that temperature has on vapor pressure of the evaporating species, the Antoine equation can be used in the following form:

$$\log p = A - \frac{B}{C+T} \tag{3}$$

In Eq. (3), A, B, and C are the Antoine constants taken in a certain temperature range for the evaporating species. For adipic acid, the values of A, B, and C in the temperature range 432–611 K are 6.97589, 2377.36, and −132.475, respectively [6]. Based on Eq. (2), p can be plotted against v, and k is equaled to the slope.

In fact, the activation energy can be calculated with aid of the Arrhenius equation.

$$\ln k_{\mathrm{evap}} = \ln A - \frac{E_{\mathrm{act}}}{RT} \tag{4}$$

In Eq. (4), the coefficient of evaporation is k_{evap} at temperature T, the Arrhenius parameter is A, the energy of activation is E_{act}, the gas constant is R, and absolute temperature is T. The Arrhenius equation is based on the assumption that once A, E_{act}, and the order of a reaction are established, these values will remain constant through the experiment. If $\ln k_{\mathrm{evap}}$ is plotted against $1/T$, the activation energy is equaled to the slope multiplied by the gas constant (R). The value of $\ln A$ is equivalent to the y-intercept.

In addition, the heat of vaporization (ΔH_{vap}) can found using the Clausius–Clapeyron equation

$$\ln p = \text{constant} - \frac{\Delta H_{\mathrm{vap}}}{RT} \tag{6}$$

A relationship between p and v has been established in Eq. (2). This relationship can be utilized to generate another form of Eq. (6).

$$\ln v = \text{constant} - \frac{\Delta H_{\mathrm{vap}}}{RT} \tag{7}$$

At this point, the vapor pressure of adipic acid has already been established. A plot of $\ln v$ versus $1/T$ will provide a slope, which is equal to $-\Delta H_{\mathrm{vap}}/R$. From the slope, ΔH_{vap} can be calculated.

2. Materials

Adipic acid, Baker® grade (Lot # 960) was obtained from J.T. Baker Chemical (99.5+%).

3. Methods

The sample was studied using a simultaneous TG–DTA unit from TA Instruments, model 2960. A platinum crucible was used to hold 6.0–9.0 mg of the sample. An empty platinum crucible was used as the reference. The inner diameter of the crucibles was 6.066 mm^2. In atmospheres of dry nitrogen flowing at rates of 50, 100, 150, 200, and 300 ml min^{-1}, the first set of experiments were conducted using a rising

temperature method over the temperature range of ambient to 300°C. The heating rate for these experiments was held constant at 5°C min^{-1}. A second set of experiments was attempted, where the flow rate was also held constant at 100 ml min^{-1}, while the heating rate was varied: 2, 5, 10, 15, and 20°C min^{-1}. An electronic flowmeter purchased from J. & W. Scientific was used to regulate the gas flow.

4. Results and discussion

The data collected from the simultaneous TG–DTA unit was interpreted into three different plots demonstrating the thermal behavior of adipic acid: weight versus time (TG), dw/dt versus time (DTG), and temperature versus time. In Fig. 1, there is a typical example of these plots superimposed for adipic acid at a heating rate of 10°C min^{-1} and a flow rate of 100 ml min^{-1}. The TG curve displays a gradual mass loss. The DTG plot of adipic acid (Fig. 1) resembled the characteristic evaporation shape and followed a zero order. The DTA plot superimposed on the TG plot shows that the evaporation occurs between the melting point and the boiling point [7]. In Fig. 2, the DTA plot for adipic acid possesses one endothermic peak in the lower temperature range and one endothermic peak in the upper temperature range. The first peak is taken to be the melting point (T_m) of the sample, and the second is the endothermic peak for evaporation. From a typical DTG plot of adipic acid shown in Fig. 1, the maximum rate of evaporation (T_f) was obtained from the peak. In adipic acid experiments where the heating rate was varied, there was a small increase in the values of T_m and T_f as the heating rate increased. When the flow rate of N_2 was increased, there was a slight variation in the values of T_m, but T_f values seem to slightly decrease. In Tables 1 and 2, the data

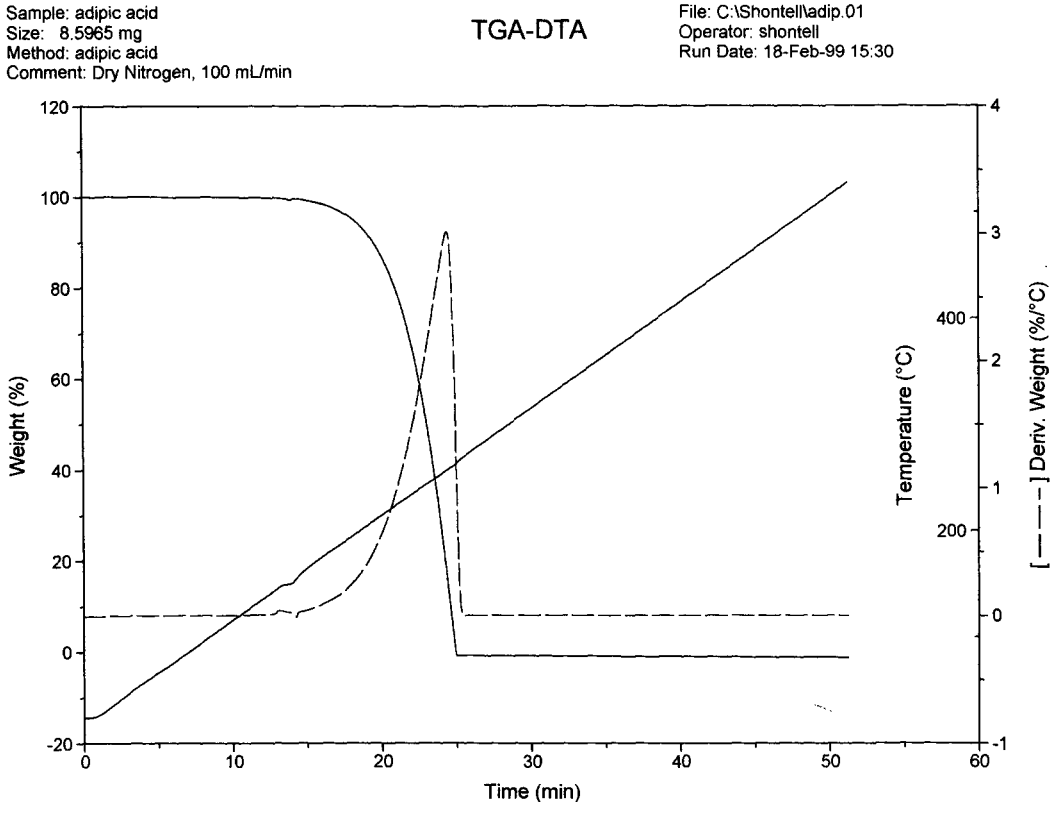

Fig. 1. The plot of mass loss versus time for adipic acid using a heating rate of 10°C min^{-1} in dry nitrogen incorporating its first derivative. The temperature versus time plot also is superimposed.

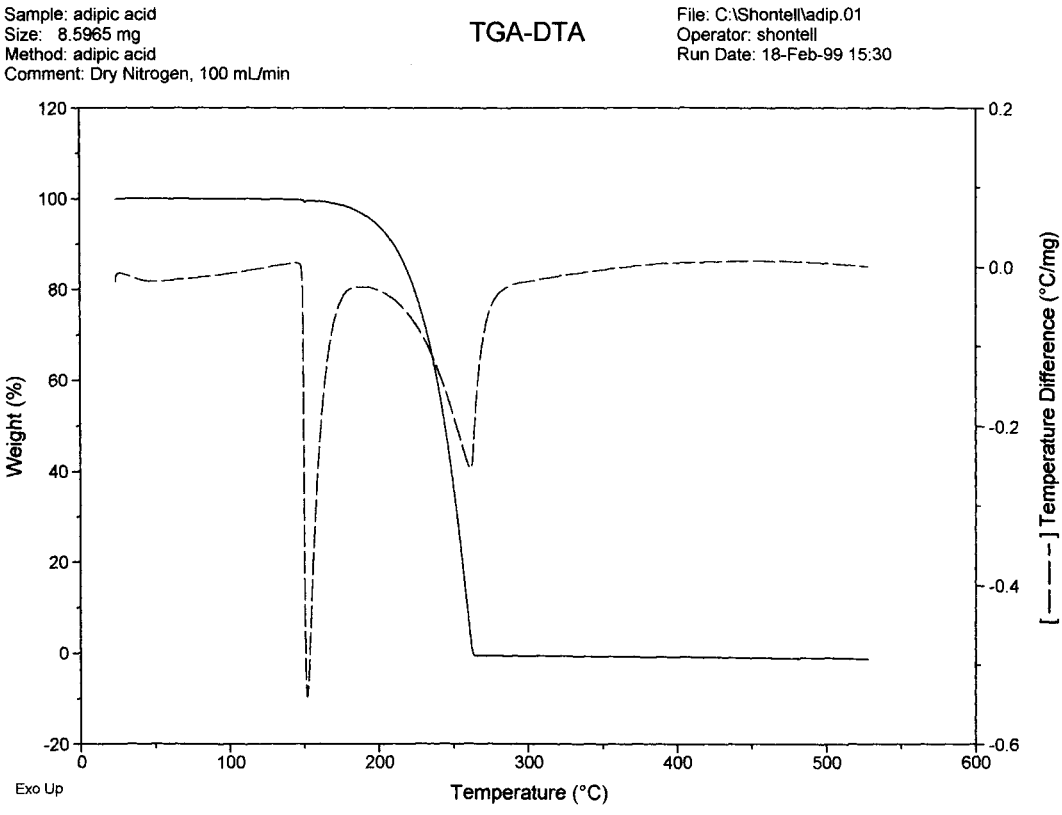

Fig. 2. The DTA and TG curves of adipic acid at a heating rate of 10°C min^{-1} in dry nitrogen.

obtained from the DTG and DTA plots based on various heating rates (β) and flow rates are listed.

Exercising the Arrhenius equation (4), the activation energy (E_{act}) of evaporation process and ln A was determined by plotting the linear relationship of the ln k_{evap} against inverse of temperature ($1/T$) in K^{-1}. From the DTG plot, the coefficient of evaporation (k_{evap}) can be taken at any temperature. E_{act} was calculated from slope, and ln A was the y-intercept. In varying heating rate experiments, the values of E_{act} and ln A were consistent. As the flow rate was increased, the E_{act} slightly decreased, where the values of ln A remained uniform. In Fig. 3, there is a sample plot of ln k_{evap} versus $1/T$ for adipic acid. The results of these determinations at different heating rates and flow rates are listed in Tables 3 and 4.

Employing the Antoine equation (3), the vapor pressure of adipic acid was calculated with respect

Table 1
Physical data at various heating rates with a flow rate of 100 ml min^{-1} of N_2

β (°C min^{-1})	T_m (°C)[a]	T_f (°C)[b]
2	151.4	224.7
5	152.2	247.1
10	152.5	265.4
15	154.1	273.0
20	156.5	282.6

[a] T_m is the melting point from the DTA plot.
[b] T_f is the rate of maximum evaporation from the DTG plot.

Table 2
Physical data at various flow rates with a heating rate of 5°C min^{-1}

Flow rate (ml min^{-1})	T_m (°C)	T_f (°C)
50	152.7	245.7
100	152.2	247.1
150	153.2	245.2
200	152.6	243.5
300	152.2	242.8

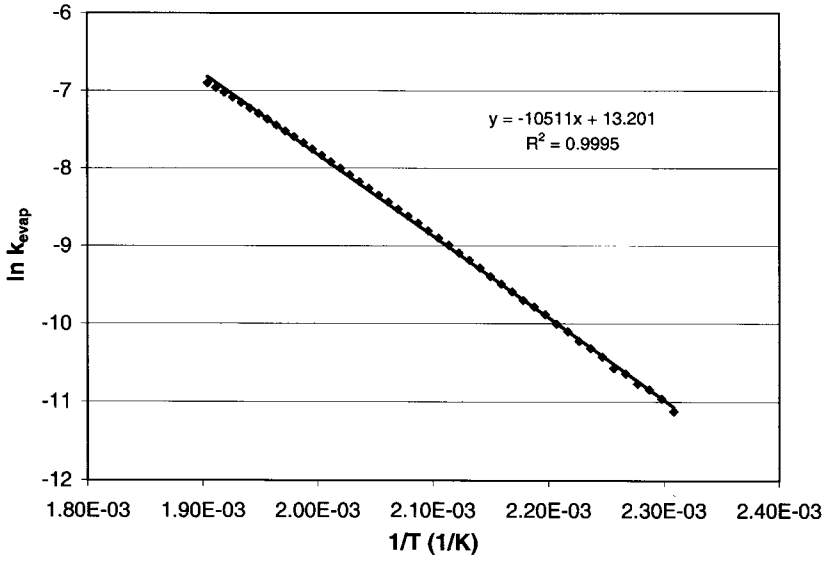

Fig. 3. The linear relationship between the natural log of the rate constant for the evaporation of adipic acid and the inverse of temperature.

Table 3
Arrhenius parameters at various heating rates[a]

β (°C min^{-1})	E_{act} (kJ mol^{-1})	ln A
2	86.9	12.9
5	87.8	13.1
10	86.9	13.1
15	86.8	12.9
20	86.4	12.8

[a] R^2 values for these linear relationships were 0.999.

Table 5
The enthalpy of vaporization at various heating rates[a]

β (°C min^{-1})	ΔH_{vap} (kJ mol^{-1})
2	88.8
5	89.7
10	88.9
15	88.8
20	88.4

[a] R^2 values for these linear relationships range were 0.999.

to temperature. A plot of vapor pressure versus v was constructed for adipic acid in order to estimate the value of k. A plot is shown in Fig. 4. There is a linear relationship achieved from this plot, and the value of k is taken to be the slope. From Fig. 4, the value of k in Eq. (2) was 1.348×10^5 with a R^2 value of 1.000.

Utilizing the Clausius–Clapeyron equation (7), the enthalpy of vaporization (ΔH_{evap}) is calculated based on the slope from the graph of ln v and 1/T.

Table 4
Arrhenius parameters at various flow rate of N_2[a]

Flow rate (ml min^{-1})	E_{act} (kJ mol^{-1})	ln A
50	88.4	13.2
100	87.8	13.1
150	87.1	13.0
200	87.3	13.1
300	86.5	12.9

[a] R^2 values for these linear relationships range from 0.998 to 0.999.

Table 6
The enthalpy of vaporization at various flow rate of N_2[a]

Flow rate (ml min^{-1})	ΔH_{vap} (kJ mol^{-1})
50	90.3
100	89.7
150	89.1
200	89.2
300	88.5

[a] R^2 values for these linear relationships range from 0.999 to 1.000.

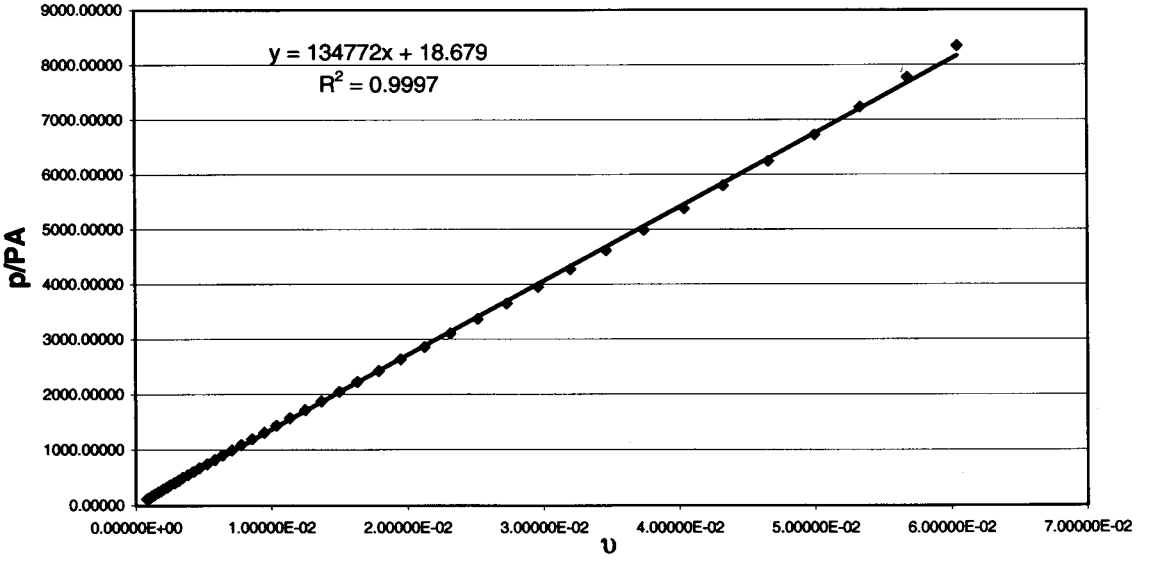

Fig. 4. The linear relationship between the vapor pressure and v of adipic acid.

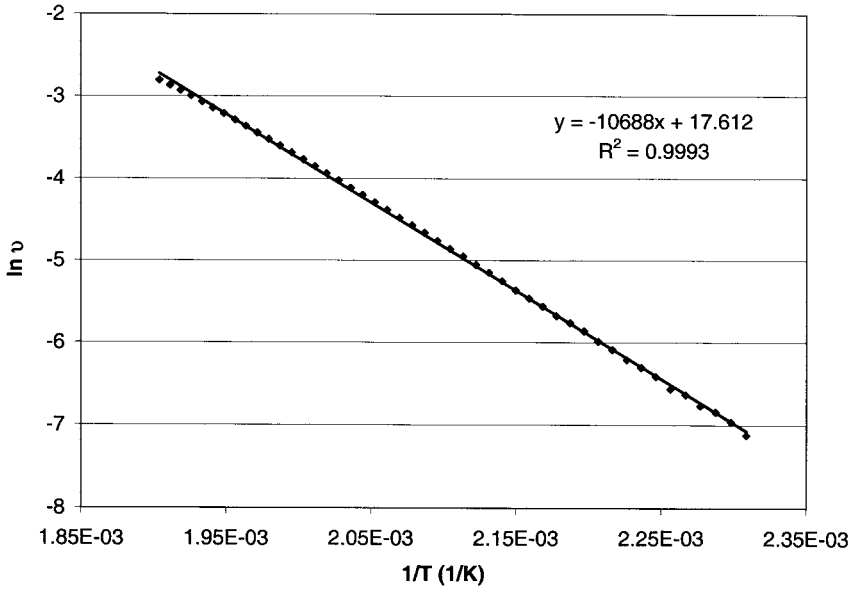

Fig. 5. The linear relationship between the natural log of v for the evaporation of adipic acid and the inverse of temperature.

Within the temperature range where the evaporation of adipic acid takes place, ΔH_{vap} should remain constant for all the experiments. A sample graph of ln v and $1/T$ for adipic acid is plotted in Fig. 5. ΔH_{vap} values are listed in Tables 5 and 6 based on experiment at varying heating rates and flow rates.

5. Conclusion

The thermal behavior of adipic acid was successfully examined using thermogravimetry. The evaporation process of adipic acid is characteristic of a zero order reaction based on the comparison of the DTG

plots of adipic acid. The process was endothermic. The evaporation of adipic acid from a constant surface area took place roughly in the temperature region 151.4–282.6°C depending on the heating rate. The experiments, where the flow rate was varied, the calculated results remained uniformed for the experiments. The activation energy varies from 86.4 to 88.4 kJ mol^{-1}. The natural log of the pre-exponential factor ($\ln A$) ranged from 12.8 to 13.1. ΔH_{vap} was calculated in the range 88.4–90.3 kJ mol^{-1}, and this range was roughly comparable to the E_{act} range determined in this study. It has been demonstrated in other evaporation studies that ΔH_{vap} and E_{act} are equal. The melting point of adipic acid did agree with the values found in literature. This investigation of adipic acid illustrates the potential value of thermal analysis in the cosmetic industry. Methods of analyzing cosmetics using thermal analysis are being developed in this laboratory and will be discussed in future reports.

References

[1] M. Balsam, E. Sagarin (Eds.), Cosmetics, Science and Technology, 2nd Edition, Krieger, Florida, 1972, pp. 291–292.
[2] R. Winter (Ed.), A Consumer's Dictionary of Cosmetic Ingredients, 3rd Edition, Crown, New York, 1989, p. 21.
[3] P. Stecher (Ed.), The Merck Index, 8th Edition, Rahway, New Jersey, 1968, p. 21.
[4] P. Aggarwal, D. Dollimore, J. Therm. Anal. 50 (1997) 526–531.
[5] D. Price, M. Hawkins, Thermochim. Acta 315 (1998) 19–24.
[6] R. Stephenson, S. Malanowski, Handbook of the Thermodynamics of Organic Compounds, Elsevier, New York, 1987, p. 194.
[7] S. Lerdkanchanaporn, D. Dollimore, J. Therm. Anal. 49 (1997) 879–886.