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Enthalpy of Vaporization of Some Organic Substances at 25.0°C and Test of Calorimeter

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In the course of the calibration of ebulliometers at around 200°C, some recommended standard substances,[1] such as aniline, methyl benzoate, and nitrobenzene, were carefully purified. For these compounds, no calorimetric data of the enthalpy of vaporization (ΔH_v) at 25.0°C have been found in the literature. On the other hand, there is some doubt whether or not it is possible to measure the ΔH_v for compounds having such a high boiling temperature by means of a calorimeter which is constructed so as to pass an inert carrier gas through its cavities in order to evaporate the substance.

An attempt was made to examine the possibilities of determining the ΔH_v-values for these low-vapor-pressure compounds and, if possible, to compare the ΔH_v-values with those calculated from their vapor pressure–temperature relations.

Experimental

Materials. Aniline, methyl benzoate, nitrobenzene, and diethylene glycol diethyl ether were employed in this investigation. All of these compounds were obtained from commercial sources and were of a puris grade (B.D.H.). Prior to the purifications, diethylene glycol diethyl ether was dried over metallic sodium,[2] whereas the standard substances were treated by shaking them over molecular sieves (4A). The compounds were purified by repeated fractional distillations under a regulated reduced pressure so as to distil the compounds at around 100°C. The best fractions collected

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[2] E. R. Alexander and A. G. Pinkus, *J. Amer. Chem. Soc.*, **71**, 1787 (1949).

Table 1. Some physical ccnstants of compounds

Compound	Boiling point (°C)	d^{25} Observed	d^{25} Reference	n_D^{25} Observed	n_D^{25} Reference
Aniline	184.00[c] 184.32[a] 184.40[b]	1.0175	1.0173[d] 1.0175[c] 1.01750[a]	1.5837	1.58364[a] 1.5840[d] 1.5855(20°)[c] 1.58318[k]
Methyl benzoate	199.35[a] 199.50[b]	1.0839	1.08377[a]	1.5147	1.51457[a]
Nitrobenzene	210.85[a,b]	1.1983	1.19805[f] 1.1982[a] 1.19864[e]	1.5500	1.55006[a]
Diethylene glycl diethyl ether	181—189[g] 186.0[j] 188.9[i] 187.4 (observed)	0.9043	0.9063(20°)[h]	1.4094	1.4155(20°)[h]

a) International Bureau of Standards. Ref. 4., Dreisbach, Ref. 15. b) Weissberger, Ref. 1. c) Deshpande *et al.*, Ref. 5. d) Average value calculated from data at 20° and 30°C, Summer *et al.*, Ref. 6. e) Walden *et al.*, Ref. 7. f) Bowden *et al.*, Ref. 8. g) Doolittle, Ref. 9. h) Value at 20°C. Vogel, Ref. 10. i) Othmer *et al.*, Ref. 11. j) Wikoff *et al.*, Ref. 12; Kotera *et al.*, Ref. 13. k) Dreisbach *et al.*, Ref. 14.

Table 2. Enthalpy of vaporization of some organic substances at 25.0°C

Exp. No.	Amount of substance evaporated (mg)	Evaporation time (sec)	Electric current supplied (mA)	Electrical energy supplied (J)	Apparent enthalpy of vaporization (kJ/mol)	Zero effect correction (kJ/mol)	Enthalpy of vaporization This work (kJ/mol)	Enthalpy of vaporization Literature value (kJ/mol)
				Aniline				
1	40.52	1213.3	20.116	24.425	56.134	−0.207	55.927	54.28[a]
2	40.40	1207.6	20.115	24.308	56.028	−0.207	55.821	
3	40.30	1205.5	20.117	24.271	56.082	−0.208	55.874	58.1[b]
4	40.33	1204.1	20.120	24.250	55.994	−0.208	55.786	
5	40.15	1206.3	20.114	24.280	55.898	−0.207	55.691	46.2[d]
6	40.19	1203.6	20.107	24.209	56.095	−0.208	55.887	
7	40.19	1202.3	20.112	24.194	56.061	−0.208	55.853	
							55.834±0.029	
				Methyl benzoate				
1	32.74	1195.6	15.028	13.435	55.869	−0.301	55.568	55.84[a]
2	32.79	1198.9	15.033	13.479	55.965	−0.305	55.660	
3	48.73	1197.5	18.304	19.960	55.764	−0.201	55.563	52.5[b]
4	49.16	1204.1	18.306	20.074	55.651	−0.197	55.454	
5	33.06	1205.6	15.037	13.562	55.898	−0.305	55.593	51.4[c]
							55.568±0.039	
				Nitrobenzene				
1	35.62	1201.7	16.397	16.074	55.551	−0.498	55.053	55.19[a]
2	35.76	1204.9	16.398	16.119	55.488	−0.498	55.990	
3	36.05	1213.0	16.396	16.223	55.555	−0.494	55.061	57.2[b]
4	38.33	1803.5	13.830	17.161	55.551	−0.502	55.049	
5	25.67	1216.2	13.830	11.593	55.497	−0.494	55.003	
							55.013±0.018	
				Diethylene glycol diethylether				
1	40.59	1217.1	15.603	14.744	58.933	−0.629	58.304	
2	39.94	1202.5	15.595	14.552	59.105	−0.639	58.466	
3	39.90	1200.2	15.599	14.532	59.091	−0.640	58.451	
4	39.97	1201.2	15.600	14.564	59.030	−0.639	58.391	
							58.403±0.037	

a) Dreisbach, Ref. 15. b) Calculated from the data of Stull, Ref. 18. c) Dreisbach *et al.*, Ref. 14. d) Calculated from the ΔH_v-values at 20° and 60°C. Arich *et al.*, Ref. 19.

were dried again over the respective desiccant and then distilled into dried 5-m*l* glass ampoules placed in a small Brühl apparatus containing Drierite on its bottom. The ampoules filled with the substances were flushed with dry nitrogen and then sealed. The purity of the samples, judged by glc, was, in all cases, shown to be 99.9 mol% or better; besides, the water content, also analysed by glc,[3] was estimated to be less than 0.015 wt%. Some physical properties of these compounds are listed in Table 1.

Calorimeter and Calorimetric Procedures. Main part of the calorimeter is made up of a hollow cylindrical silver vessel. Details of the construction of the calorimeter and of the calorimetric procedures have been described elsewhere.[16–18]

In the course of the experimental determinations of methyl benzoate and aniline, the electrical energy supplied to the calorimeter and/or the evaporation time has been altered in order to determine whether or not the ΔH_v-values observed are affected by such experimental conditions. However, the influence of neither the electrical energy nor the evaporation time was observed in any cases, as may be seen in Table 2.

Results and Discussion

The results of the calorimetric determinations are summarised in Table 2. Since the uncertainties accompanying the average values of ΔH_v, given by the standard deviations, are found to be less than 40 J/mol, the reproducibility of each experimental run is considered to be quite satisfactory. However, in the present cases, since the correction terms,[16–18] most of which consist of an zero-effect correction which is estimated to contain a error of more than 10% in itself, amount to several hundred joules at the highest, the uncertainty caused by the correction terms serves to decrease the accuracy of each observed ΔH_v-value. In addition to this, since some systematic errors decrease the accuracy, it is advisable to round the last significant figures in each average ΔH_v-value.

The observed ΔH_v-values for methyl benzoate and for nitrobenzene gave an excellent agreement with the respective literature values compiled by Dreisbach;[15] on the contrary, for aniline, a result higher than the literature value[15] by 1.55 kJ/mol was observed. The ΔH_v-values evaluated from the vapor pressure-temperature relation,[20] using data compiled by Stull,[21] gave poor agreement in all cases. No ΔH_v datum for diethylene glycol diethyl ether could be found in the literature, but that determined in this investigation is acceptable since the plot of the ΔH_v-value *versus* the normal boiling temperature falls on a point to be expected from the same relations of 1,2-dialkoxyethanes and 2-alkoxyethyl acetates[17] and of a homologous series of $C_2H_5(OCH_2)_nCH_3$.[22]

From the experimental results, it can be concluded that a calorimeter of this type can be used for the determination of the enthalpy of vaporization at 25.0°C for compounds with normal boiling temperature up to 210°C.

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