

# HEATS OF VAPORIZATION OF BINARY AZEOTROPIC MIXTURES CONTAINING ALIPHATIC ALCOHOLS AND HYDROCARBONS\*

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Received September 16th, 1976

Temperature dependences of heats of vaporization of binary mixtures azeotropic benzene-methanol, benzene-ethanol, benzene-propanol, cyclohexane-methanol, cyclohexane-ethanol, cyclohexane-propanol, cyclohexane-butanol, and cyclohexane-methanol systems were determined at 40 to 80°C. The experimental data were used for analyzing the possibility of estimation of the heat of vaporization in the vicinity of the boiling point.

Heats of vaporization of azeotropic mixtures constitute one of interesting fields in thermodynamics. Since differential, integral, isobaric, and isothermal heats of vaporization are for such mixtures identical, from the experimental point of view they represent the most simple measurable mixture of corresponding substances. Besides other things, this is significant also due to the fact that it enables to use the experimental equipment designed for determining heats of vaporization of pure substances. Since, theoretically, the thermodynamics of azeotropic mixtures is elaborated to considerable detail, it seems suitable to investigate their experimental properties experimentally and to employ the results for the description of properties whose experimental determination is still difficult.

## EXPERIMENTAL

### Preparation and Properties of Pure Substances

*Methanol* was dried by rectification, refluxed with Grignard's reagent for 6 h and finally rectified on a 1.5 m — long column packed with stainless saddles. Final values of the physico-chemical constants were equal to:  $t_{\text{NBP}}$  64.56°C,  $d_4^{25}$  0.7866,  $n_D^{25}$  1.3266, 0.01 wt.% H<sub>2</sub>O by the Fischer method and 0.01 wt.% of impurities by mass spectrometer.

*Ethanol*, the finest A.R. grade, was shaken for 2 days with annealed CuSO<sub>4</sub>, decanted, and rectified on a 1.5 m — long column packed with stainless saddles. It was being entrapped into a condensate receiver filled partially with Nalsit A4 molecular sieves. ( $t_{\text{NBP}}$  78.3°C,  $d_4^{25}$  0.7851,  $n_D^{25}$  1.3596, H<sub>2</sub>O 0.001 wt.%, impurities 0.03%).

\* Part X in the series Enthalpy Data of Liquids; Part IX: This Journal 42, 1755 (1977).

*Propanol*, A.R. grade, was refluxed for 6 h with metallic sodium, rectified on a 40-plate bubble cap column and entrapped into a receiver containing Nalsit A4 molecular sieves. ( $t_{\text{NBP}}$  97.2°C,  $d_4^{20}$  0.80347,  $n_D^{23.6}$  1.3840, H<sub>2</sub>O 0.005 wt.%, impurities 0.01%).

*Butanol*, A.R. grade, was refluxed for 6 h with metallic sodium, rectified on a 40-plate bubble cap column and entrapped into a receiver containing Nalsit A4 molecular sieves. ( $t_{\text{NBP}}$  118.0,  $d_4^{25}$  0.8057,  $n_D^{25}$  1.3973, H<sub>2</sub>O 0.003 wt.%, impurities 0.01%).

*Benzene*, thiophene-free A.R. grade, was rectified with metallic sodium on a 1.5 m — long column packed with stainless saddles. ( $t_{\text{NBP}}$  80.10°C,  $d_4^{25}$  0.87368,  $n_D^{25}$  1.4979, H<sub>2</sub>O 0.007 wt.%, impurities 0.01%).

*Cyclohexane*, A.R. grade, was rectified on a 40-plate bubble cap column and entrapped into a receiver with Nalsit A4 molecular sieves. ( $t_{\text{NBP}}$  80.7°C,  $d_4^{25}$  0.7739,  $n_D^{25}$  1.4236, H<sub>2</sub>O 0.003 wt.%, impurities 0.01%).

*Cyclohexene* was prepared by dehydration of cyclohexanol with concentrated H<sub>2</sub>SO<sub>4</sub> (ref.<sup>1</sup>) The product was distilled off from the reaction mixture at a reflux of 1 : 2, mixed with CaH<sub>2</sub> and rectified again in nitrogen atmosphere at a reflux of 1 : 5. The distillate was entrapped into a receiver with Nalsit A4 molecular sieves. ( $t_{\text{NBP}}$  83.01°C,  $d_4^{20}$  0.8110,  $n_D^{20}$  1.4467, H<sub>2</sub>O 0.004 wt.%, impurities 0.01%).

The measured values of the physico-chemical constants of all components were in good agreement with literature data<sup>2</sup>.

#### Description of the Apparatus and Working Procedure

The measurements were performed on an isothermal adiabatic calorimeter with a closed circuit and working at the pressure of saturated vapours. The whole apparatus has been described in detail earlier<sup>3,4</sup>. Heats of vaporization of azeotropic mixtures were calculated from the relation

$$\Delta H_{v,az} = (h_1 - h_2 - h_3)/m, \quad (1)$$

where  $\Delta H_{v,az}$  is the heat of vaporization of the azeotropic mixture,  $h_1$  is the total heat delivered into the calorimeter,  $h_2$  the correction for the calorimeter run,  $h_3$  the correction for the increase of the vapour space after evaporation of  $m$  grams of the substance at temperature  $T$ .

#### Preparation of Azeotropic Mixtures

Any azeotropic mixture of required composition can be prepared essentially in two ways. Either a suitable experimental method can be employed (*e.g.* ebulliometer<sup>5</sup> or a rectification column) or we can calculate the azeotropic composition and the boiling point from accurate vapour-liquid equilibrium data by using a proper correlation method and prepare subsequently such a mixture by weighing.

In our work we decided to use the latter method. In the first place, by analyzing experimental methods we arrived at a conclusion that both the experimental and computational methods yield data with approximately the same error and, moreover, the necessity to prepare relatively large amounts of azeotropic mixtures makes this method easier and faster. According to our experience we selected the Wilson equation for calculating the composition of azeotropic mixtures. Calculated values of the composition, boiling point, and vapour pressure are given in first columns of Table I. All the data agree well with those reported in the literature<sup>6,7</sup>.

## RESULTS

Measured values of the heat of vaporization of all azeotropic mixture are summarized in the last column of Table I. The reported values of  $\Delta H_{v,az}$  are mean values from 3–5 experimental measurements with the standard deviation lower than 0.2%.

TABLE I  
Experimental Values of Heat of Vaporization

Composition	Temperature, °C	Pressure, kPa	$\Delta H_{v,az}$ , kJ mol
benzene-methanol			
0.440	28.86	29.73	35.000
0.425	35.00	39.32	34.748
0.411	41.96	53.32	34.229
0.412	45.00	60.39	34.359
0.397	51.90	80.79	33.765
0.399	55.00	90.39	33.899
0.392	57.17	98.65	33.765
0.387	57.70	101.32	33.505
benzene-ethanol			
0.602	51.02	53.32	34.350
0.589	55.00	62.39	34.405
0.573	60.00	75.72	33.982
0.571	61.50	80.79	34.007
0.555	67.50	98.65	33.744
0.567	67.70	101.32	33.920
benzene-propanol			
0.867	45.00	31.99	33.464
0.856	50.00	38.92	33.288
0.839	58.29	53.32	32.882
0.825	65.00	68.52	32.744
0.803	69.70	80.79	32.547
0.801	76.30	99.99	32.321
cyclohexane-methanol			
0.402	49.10	80.79	33.271
0.424	50.00	80.79	33.928
0.395	54.10	98.65	33.012
0.394	54.70	101.32	32.974
0.410	55.00	103.85	33.526

TABLE I  
(Continued)

Composition	Temperature, °C	Pressure, kPa	$\Delta H_{v,az}$ , kJ
cyclohexane-ethanol			
0.609	48.52	53.32	34.681
0.605	50.00	57.06	34.505
0.589	54.70	68.52	34.325
0.574	58.70	80.79	34.095
0.559	64.70	101.32	33.823
0.557	65.00	102.25	33.836
cyclohexane-propanol			
0.809	55.0	51.19	33.321
0.905	56.36	53.32	33.179
0.789	65.00	73.05	33.087
0.779	67.90	80.79	32.978
0.749	74.40	101.32	32.334
cyclohexane-butanol			
0.943	50.00	38.26	32.054
0.927	60.11	53.32	31.698
0.912	70.00	74.52	30.999
0.903	72.90	80.79	30.794
0.897	79.40	101.32	30.468
cyclohexene-methanol			
0.400	46.58	68.52	34.765
0.391	50.3	80.82	34.597
0.381	55.05	98.66	34.351

Heat of mixing is one of most important quantities characterizing liquid mixtures. However, at temperatures approaching the boiling point its experimental determination becomes extremely difficult and, as a result, these data are often missing in the literature. Thus, the knowledge of heats of vaporization of such mixtures represents one of possibilities of its estimation. Considering that the liquid molar volume is negligible and the ratio of fugacity coefficients  $\varphi_i = v_i^0(T, P_i^0)/v_i(T, P, y)$  is independent of temperature, the following relations holds

$$\Delta H_v = y_1 \Delta H_{v,1} \left( \frac{z^{\#}}{z_1^{\#}} \right) + y_2 \Delta H_{v,2} \left( \frac{z^{\#}}{z_2^{\#}} \right) - z^{\#}(y_1 L_1 + y_2 L_2), \quad (2)$$

where  $\Delta H_{v,i}$  is the heat of vaporization of the pure component and  $L_i$  is the partial molar heat of mixing.

Since

$$L_1 = H^E + x_2(\partial H^E/\partial x_1), \quad L_2 = H^E - x_1(\partial H^E/\partial x_1)$$

it holds

$$y_1 L_1 + y_2 L_2 = H^E + (y_1 - x_1)(\partial H^E/\partial x_1), \quad (3)$$

which enables to rewrite relation (2) into the form

$$H^E + (y_1 - x_1)(\partial H^E/\partial x_1) = (y_1 \Delta H_{v,1} \psi_1 + y_2 \Delta H_{v,2} \psi_2 - \Delta H_v)/z^{\#}, \quad (4)$$

where

$$\psi_i = z^{\#}(T, P, y)/z_i^{\#}(T, P_i^0),$$

and which, at the azeotropic point, assumes the form of

$$H_{az}^E = (x_{1,az} \Delta H_{v,1} \psi_1 + x_{2,az} \Delta H_{v,2} \psi_2 - \Delta H_{v,az})/z^{\#}. \quad (5)$$

Both simplifications introduced are well justifiable. The first one due to the relation  $v^1 \ll v^{\#}$  which holds in the vicinity of the boiling point. The correctness of the assumption of the temperature independence of the fugacity coefficient ratio follows then from the relation

$$|d \ln \varphi_i/dT| \ll d \ln P_i^0/dT, \quad (6)$$

whose validity may be easily proved.

In the calculation itself, the state behaviour of both the pure components and the mixture was approximated by second virial coefficients whose values were taken from the literature<sup>8</sup> for the benzene-methanol system or, due to the lack of experimental data on the other systems, they were determined by the O'Connell and Prausnitz method<sup>9</sup>. Estimated values of the heat of mixing<sup>10</sup> of separate systems are given in the third column of Table II with the exception of the cyclohexane-methanol system, where the azeotropic mixture is heterogeneous, and the cyclohexane-methanol system, where experimental data are not available.

A comparison between experimental and calculated data is relatively difficult. Experimental values of the heat of mixing are known above all at 25°C or at mildly

elevated temperatures. For temperatures near the boiling point, the calculated values can be compared only with those obtained by extrapolation of experimental

TABLE II  
Calculated and Experimental Values of  $H^E$  (J/mol)

Temperature °C	Compo- sition	$H_{calc}^E$	$H_{exp}^E$	$\delta$ , %
benzene-methanol				
25.0	0.448	546	581	6.0
28.86	0.440	572	608	5.9
30.0	0.437	575	620	7.2
35.0	0.425	598	658	9.1
40.0	0.415	614	698	12.0
45.0	0.404	623	742	16.0
benzene-ethanol				
35.0	0.653	1 132	1 020	-10.9
45.0	0.621	1 221	1 161	-5.2
50.0	0.605	1 251	1 233 <sup>a</sup>	-1.4
55.0	0.589	1 272	1 276 <sup>a</sup>	0.3
60.0	0.573	1 283	1 310 <sup>a</sup>	2.0
65.0	0.557	1 284	—	—
70.0	0.540	1 274	—	—
benzene-propanol				
25.0	0.908	744	705	-5.5
35.0	0.887	905	877	-3.1
45.0	0.867	1 045	1 035	-1.0
50.0	0.856	1 105	1 112 <sup>a</sup>	0.6
55.0	0.845	1 161	1 172 <sup>a</sup>	0.9
60.0	0.835	1 210	1 228 <sup>a</sup>	1.5
65.0	0.825	1 253	—	—
70.0	0.814	1 289	—	—
75.0	0.803	1 318	—	—
cyclohexane-ethanol				
50.0	0.605	332	—	—
55.0	0.589	414	—	—
60.0	0.573	486	—	—
65.0	0.557	546	—	—

TABLE II  
 (Continued)

Temperature °C	Compo- sition	$H_{\text{calc}}^E$	$H_{\text{exp}}^E$	$\delta, \%$
cyclohexane-propanol				
55.0	0.809	555	950	41.5
60.0	0.791	726	1 060 <sup>a</sup>	31.5
65.0	0.789	886	1 165 <sup>a</sup>	24.0
70.0	0.756	1 035	1 270 <sup>a</sup>	18.5
75.0	0.739	1 172	1 375 <sup>a</sup>	14.8
cyclohexane-butanol				
50.0	0.943	668	670 <sup>a</sup>	0
55.0	0.935	801	800 <sup>a</sup>	0
60.0	0.927	928	930 <sup>a</sup>	0
65.0	0.920	1 049	1 050 <sup>a</sup>	0
70.0	0.912	1 166	1 165 <sup>a</sup>	0
75.0	0.904	1 276	1 275 <sup>a</sup>	0
80.0	0.897	1 380	1 380 <sup>a</sup>	0

<sup>a</sup> Extrapolated values.

data from much lower temperatures. This is further complicated by the fact that in some cases the value of the heat of mixing is known only at one temperature<sup>11</sup> (cyclohexane-ethanol) or that the azeotropic point is shifted to one of the concentration limits, where the concentration dependence of the heat of mixing is extremely steep and its relative error is maximal<sup>12</sup> (cyclohexane-propanol, cyclohexane-butanol). This means that agreement of such a comparison depends on the accuracy of the data, above all on values of the second virial coefficient of pure substances and the mixture. Taking into account that an *a priori* analysis gave approximately a 30fold increase in the relative error of the heat of mixing in comparison to the error in the heat of vaporization, the achieved agreement may be considered as satisfactory and the method proposed for estimating the heat of vaporization in the vicinity of  $t_{\text{NBP}}$  as feasible. This also justifies the intention to employ measurements of heats of vaporization of mixtures for constructing the concentration dependence of heat of mixing in the whole concentration range.

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Translated by K. Hlavatý.