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CALORIMETRIC SEARCH FOR RELIABLE EXCESS ENTHALPY DATA AS A FUNCTION OF TEMPERATURE

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In the search of a useful method for determining excess enthalpies as a function of temperature Calvet calorimetry was employed. To this end, excess molar enthalpies H_m^E at 298.15 and 333.15 K and excess molar heat capacities $C_{p,m}^E$ within 283.15–333.15 K were determined for the 1-decanol+*n*-decane system over the whole composition range. An isothermal flow Calvet-type calorimeter was used for H_m^E measurements, whereas $C_{p,m}^E$ were determined by means of a Setaram Micro DSC calorimeter. Excess enthalpies within 283.15–333.15 K were indirectly obtained through the integration of $C_{p,m}^E$ (T) data using H_m^E at 298.15 K. The results obtained at 333.15 K agreed with those determined directly, implying the thermodynamic consistency of the measured data and, therefore, the reliability of the indirect method.

Keywords: *Calvet calorimetry, excess enthalpies, excess heat capacities, thermodynamic consistency*

Introduction

Besides its per se interest, the heat of mixing or excess enthalpy H_m^E of liquid mixtures plays an important role in the application of a number of molecular models. Like for any other input quantity, the knowledge of H_m^E as a function of temperature and pressure is of high assistance with a view to improve the reliability of the values of the model parameters. In this respect, its temperature dependence is particularly relevant, as $(\partial H_m^E/\partial p)_T$ is very small for liquids.

Reliable H_m^E data comes from experimentation [1, 2]. Among others, Calvet calorimetry is widely recognized as a useful tool for determining H_m^E [3, 4]; however, obtaining data at various temperatures is labour-expensive and time-consuming. This is the reason why the majority of studies contain data at a single, near-ambient temperature [5–7].

An alternative approach to determine $H_m^E(T)$ entails the use of excess heat capacities $C_{p,m}^E=(\partial H_m^E/\partial T)_p$

$$H_m^E(T)=H_m^E(T_0)+\int_{T_0}^{T} C_{p,m}^E(T)\mathrm{d}T \qquad (1)$$

Then, H_m^E can be obtained in the same temperature range as $C_{p,m}^E$ once data at a reference temperature T_0 are provided. The use of Eq. (1), namely the indirect method, should be a powerful way to obtain $H_m^E(T)$ if good-quality $C_{p,m}^E(T)$ data are available. In this context, Setaram Micro DSC calorimeters – a class of Calvet calorimeters – have been shown to provide highly–accurate $C_{p,m}^E(T)$ [8–11].

The aim of this work is to check the reliability of the indirect method for obtaining $H_m^E(T)$. For this purpose, an isothermal flow Calvet–type calorimeter and a Setaram Micro DSC II calorimeter were employed to determine H_m^E at 298.15 and 333.15 K and $C_{p,m}^E$ from 283.15 to 333.15 K for the 1-decanol+*n*-decane system over the whole composition range. The selection of this system is justified from the high normal boiling points of the pure liquids, which prevents for evaporation risks in the H_m^E measurements at 333.15 K. The results are analysed and discussed after the description of the experimental procedures. Special attention is placed on the agreement between directly determined H_m^E's and those obtained from Eq. (1).

Experimental

1-Decanol (over 99% pure) and *n*-decane (over 99% pure) were purchased from Aldrich and Sigma, respectively. Both were degassed prior to use, whereas 1-decanol was dried over Fluka type 0.4 nm molecular sieves. Mixtures were prepared by weighing using a Mettler AE-240 balance. The estimated uncertainty in the mole fraction was ±0.0001.

A description of the Calvet calorimeter as well as the experimental technique for obtaining excess molar enthalpies can be found elsewhere [4]. The primary part of the calorimeter is constituted by two identical cells located inside a calorimetric block that determines their temperature. The mixing process is carried out in one of the cells (laboratory), while the other one (reference) holds a substance of similar heat capacity. The calorimetric signal is the differential heat flux ϕ,

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which is recorded during the experiment. The calorimetric block is large-sized implying high thermal inertia. This allows a good temperature stability; however, long-time stabilization periods are required. The temperature of the calorimetric block is controlled to ±0.002 K by means of an external circuit, which allows to operate from ambient temperature to 343.15 K. The signal calibration was undertaken using a Joule effect cell. Using this procedure, the uncertainty in H_m^E was estimated to be better than 2% at near–ambient temperatures, whereas it increases up to 4% for high temperatures owing to inherent experimental difficulties to these experimental conditions.

Detailed information about Micro DSC calorimeters as well as the experimental technique for determining excess molar heat capacities was made previously [8–10]. In spite of its name, this apparatus is not a conventional differential scanning calorimeter. In fact, its primary structure is identical to that of a 'classical' Calvet calorimeter; however, the small size of the calorimetric block incorporates a very effective temperature control. The calorimeter provides the heat capacity per unit volume C_pV^{-1}. Heat flow calibration was accomplished using standard liquids. Information on the calibration procedure can be found elsewhere [10]. Basically, C_pV^{-1} is obtained from

$$C_pV^{-1}=A+B\phi \tag{2}$$

where ϕ is the differential heat flow corresponding to a temperature change; in this work, temperature was varied continuously (scanning method) at a scanning rate of 0.25 K min^{-1}. The calibration constants (A and B) in Eq. (2) are usually obtained using two heat capacity standards. In this work, the number of standards was increased, the quality of the calibration was improved as a result. In particular, during calibration, the reference cell was always filled with 1-butanol, while the measuring cell held 1-butanol, 1-hexanol, *n*-tetradecane, *n*-heptane, and toluene. The C_pV^{-1} values for them were obtained from compilations of isobaric molar heat capacities $C_{p,m}$ [12, 13] and densities ρ [14, 15] using the relation

$$C_{p,m}=\frac{M_w}{\rho}C_pV^{-1} \tag{3}$$

where M_w denotes the molecular mass. Obviously, density data ρ are necessary with a view to obtain $C_{p,m}$. An Anton-Paar DSA-48 vibrating–tube density meter – accurate to ±0.0001 g cm^{-3}– was used to this end, and a detailed description of the experimental method can be found elsewhere [16]. Using this procedure, the uncertainty in $C_{p,m}$ was quoted to ±0.2 J mol^{-1} K^{-1}, whereas that in $C_{p,m}^E$ was ±0.05 J mol^{-1} K^{-1} because of cancellation of systematic errors.

Results and discussion

Table 1 contains the directly determined H_m^E at 298.15 and 333.15 K. These data are plotted in Fig. 1. As it can be seen, data at 298.15 K are in good agreement with previously reported values [17] while, as expected ('Experimental'), data at 333.15 K are of

Table 1 Directly determined excess molar enthalpies H_m^E for x1-decanol+(1–x)n-decane at the temperature T

x	H_m^E /J mo1^{-1} T=298.15 K	x	H_m^E /J mo1^{-1} T=333.15 K
0.0180	226	0.0190	256
0.0392	256	0.0550	710
0.0599	352	0.0704	747
0.0978	433	0.0728	748
0.0910	404	0.0930	804
0.1088	477	0.2026	1012
0.2030	530	0.2990	1013
0.3034	550	0.3979	972
0.4035	543	0.4983	929
0.4515	540	0.5080	839
0.4989	508	0.5574	815
0.5433	493	0.6107	699
0.5950	452	0.6752	579
0.6932	380	0.7120	552
0.7962	266	0.7921	443
0.8977	138	0.7924	475
0.9419	78	0.8930	192
		0.9402	108

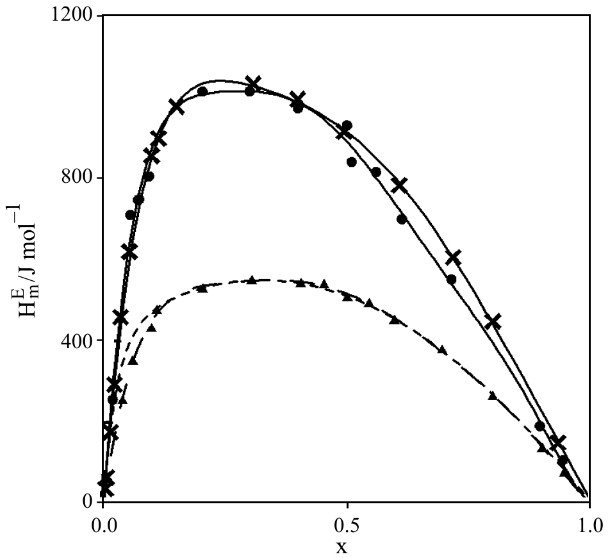

Fig. 1 Excess molar enthalpies H_m^E for x1-decanol+(1–x)n-decane. Directly determined data at ▲ – T=298.15 K and ● – T=333.15 K. Indirectly determined data at × – T=333.15 K. —– Fitted values to Eq. (4); --- – literature data at T=298.15 K [17]

lower quality. The solid lines are the fitted values to a polynomial on the form

$$Y_m^E = x(1-x)\frac{\sum_{i=1}^{n} A_i (2x-1)^{i-1}}{1+\sum_{j=0}^{m} B_j (2x-1)^{j}} \tag{4}$$

where Y=H and A_i and B_j are the fitting coefficients. Table 2 contains the final results of the fitting; it must be pointed out that no results for B_j are given as they were statistically insignificant in this particular case. Table 3 shows $C_{p,m}^E$ from 283.15 to 333.15 K every 10 K. They are represented in Fig. 2a together with the fitted values to Eq. (4) – with Y=C_p. The values of the fitting coefficients are listed in Table 4. Data at 298.15 K are also given in Table 3 and represented in Fig. 2b. As it can be observed, they agree closely with their reported counterparts [18].

In order to obtain the H_m^E values from the indirect method, i.e. Eq. (1), $C_{p,m}^E$ data at each composition were fitted to the following polynomial

Table 2 Fitting coefficients of Eq. (4) to directly determined excess molar enthalpies and standard deviations σ

A_1	A_2	A_3	A_4	A_5	A_6	σ
			T=298.15 K			
2062	–953.8	347.8	–332.5	2395	–2482	8
			T=333.15 K			
3548	–2630	414.5	848.9	5048	–6503	35

Table 3 Excess isobaric molar heat capacities $C_{p,m}^E$ for x1-decanol+(1–x)n-decane at the temperature T

x	$C_{p,m}^E$/J mol^{-1} K^{-1}						
	283.15 K	293.15 K	298.15 K	303.15 K	313.15 K	323.15 K	333.15 K
0.0044	0.36	–0.07	–0.19	–0.29	–0.34	–0.35	–0.36
0.0064	1.69	0.94	0.56	0.18	–0.11	–0.31	–0.41
0.0150	3.64	3.43	3.06	2.48	1.22	0.16	–0.37
0.0226	4.94	5.19	5.09	4.71	3.50	1.89	0.45
0.0351	5.91	6.69	6.94	6.96	6.41	5.01	3.00
0.0530	6.68	7.83	8.30	8.58	8.77	8.12	6.39
0.0984	7.54	9.21	9.94	10.7	11.8	12.5	12.1
0.1128	7.62	9.37	10.3	11.0	12.4	13.3	13.3
0.1497	7.98	9.81	10.7	11.7	13.3	14.7	15.3
0.3068	7.65	9.54	10.5	11.5	13.4	15.4	17.1
0.3978	7.24	8.89	9.78	10.7	12.5	14.4	16.2
0.4925	6.46	7.86	8.65	9.37	10.9	12.6	14.3
0.6053	5.59	6.60	7.26	7.73	8.95	10.2	11.7
0.7157	4.52	5.25	5.63	5.97	6.72	7.66	8.60
0.7967	3.50	3.99	4.26	4.59	5.07	5.67	6.19
0.9298	1.01	1.24	1.40	1.51	1.67	1.86	2.03

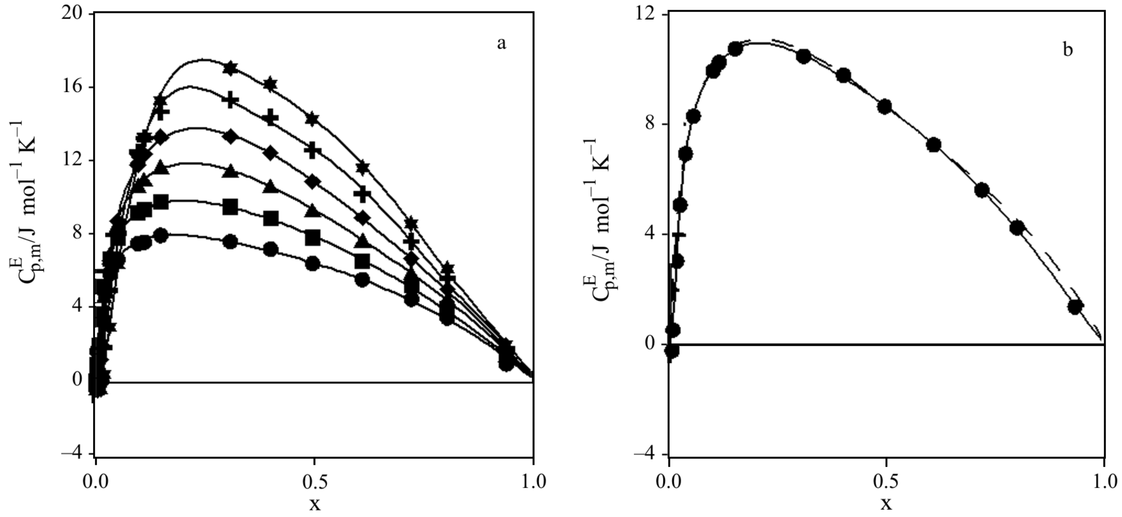

Fig. 2 Excess molar heat capacities $C^{E}_{p,m}$ for x1-decanol+(1–x)n-decane. a – Data at ● – T=283.15 K, ■ – T=293.15 K, ▲ – T=303.15 K, ◆ – T=313.15 K, ✚ – T=323.15 K, ✱ – T=333.15 K. b – Data at ● – T=298.15 K; --- – literature data at T=298.15 K [18]; — – fitted values to Eq. (4)

Table 4 Fitting coefficients of Eq. (4) to excess molar heat capacities and standard deviations σ

A_1	A_2	A_3	A_4	A_5	A_6	B_1	B_2	B_3	σ
T=283.15 K									
25.81	9.498	4.559				0.9411			0.4
T=293.15 K									
31.54	44.37	14.90	4.033	1.788		2.082	1.194	0.1124	0.2
T=298.15 K									
34.39	45.45	15.16	4.857	–10.23	–10.83	1.994	0.9950		0.1
T=303.15 K									
37.32	46.44	9.164	7.367	7.065		2.004	1.028	0.0237	0.2
T=313.15 K									
43.32	67.48	24.31	7.298			2.352	1.706	0.3524	0.2
T=323.15 K									
50.33	16.77	–7.151	–41.25	–8.162	64.49	0.9899			0.5
T=333.15 K									
56.84	16.71	–7.866	–38.57	–17.34	62.50	0.9652			0.4

$$C^{E}_{p,m} = \sum_{i=1}^{n} A_i T^{i-1} \qquad (5)$$

The fitting coefficients A_i as well as the standard deviations can be found in Table 5. In the application of Eq. (1), T_0=298.15 K was taken as the reference temperature. Thus, for each composition, the fitted $H^{E}_{m}(T_0)$ value was used, integration of the $C^{E}_{p,m}(T)$ polynomials gave rise to H^{E}_{m} in the 283.15–333.15 K range as a result. These data can be found in Table 6 every 10 K intervals and they are represented in Fig. 3 together with the fitted curves to Eq. (4). All relevant information concerning the fitting results is given in Table 7.

Finally, Fig. 1 also shows comparison between H^{E}_{m} at 333.15 K as obtained directly and from the indirect method. It is worth-noting that both sets of data are mutually consistent implying the thermodynamic consistency of all measured data. Although directly measured H^{E}_{m} at 333.15 K are reasonably good, the indirect method is found to provide more reliable H^{E}_{m} – higher internal consistence of data as a function of composition is found for the latter dataset. In fact, it appears that the uncertainty in the second term of the right-hand side in Eq. (1) is small. Therefore, it can be concluded that the indirect methodology presented here is a powerful way to determine the excess enthalpy as a function of temperature.

Table 5 Fitting coefficients of Eq. (5) and standard deviations σ

x	A_1	A_2	A_3	A_4	A_5	σ
0.0044	3.96E2	–3.69	1.42E–2	–1.18E–5		0.03
0.0064	– 47.15	0.09	–0.004	5.41E–6		0.07
0.0150	–1.61E–5	–6.79	6.70E–2	–2.19E– 4	2.37E–7	0.05
0.0223	–8.47E1	– 4.19	4.51E–2	–1.47E– 4	1.55E–7	0.07
0.0351	1.14E2	–2.12	1.05E–2	–1.55E–5		0.06
0.0530	6.50E–6	1.46	–1.74E–2	6.77E–5	–8.56E–8	0.04
0.0984	3.85E–4	2.32	–2.54E–2	9.17E–5	–1.08E–7	0.04
0.1128	3.87E–4	2.02	–2.23E–2	8.10E–5	–9.58E–8	0.04
0.1497	3.87E–4	2.03	–2.20E–2	7.85E–5	–9.11E–8	0.04
0.3076	3.77E–4	3.29E–1	– 4.40E–3	1.78E–5	–2.14E–8	0.05
0.3978	3.80E–4	5.14E–1	–5.82E–3	2.12E–5	–2.37E–8	0.04
0.4925	1.14E–3	–9.04E–2	4.00E– 4			0.04
0.6053	3.73E–4	–5.32E–1	5.00E–3	–1.58E–5	1.76E–8	0.04
0.7156	– 4.89E–6	–7.50E–1	7.31E–3	–2.37E–5	2.63E–8	0.04
0.7974	3.70E–4	–9.83E–1	9.43E–3	–3.00E–5	3.23E–8	0.05
0.9298	3.19E–4	– 4.63E–2	2.81E– 4	–3.69E–7		0.04

Table 6 Indirectly determined excess molar enthalpies H_m^E for x1-decanol+(1–x)n-decane at the temperature T

x	H_m^E/J mol^{-1}					
	283.15 K	293.15 K	303.15 K	313.15 K	323.15 K	333.15 K
0.0044	49	50	48	45	41	37
0.0064	53	66	71	72	69	66
0.0150	88	124	154	172	179	177
0.0226	113	165	215	256	283	294
0.0351	161	224	293	360	418	459
0.0530	218	291	374	461	546	619
0.0984	311	395	495	608	731	855
0.1128	331	416	518	635	764	897
0.1497	363	452	559	685	825	975
0.3068	411	497	601	726	869	1031
0.3978	414	494	591	707	841	994
0.4925	404	475	561	663	780	914
0.6053	361	422	494	577	673	782
0.7157	283	332	389	452	524	605
0.7967	207	245	288	336	389	448
0.9298	71	82	96	112	130	149

Table 7 Fitting coefficients of Eq. (4) to indirectly determined excess molar enthalpies and standard deviations σ

A_1	A_2	A_3	A_4	A_5	B_1	σ
			T=283.15 K			
1583	711.8	24.00			0.87	10
			T=293.15 K			
1869	826.8	50.74			0.89	8
			T=303.15 K			
2232	1013	93.57	–718.5	–288.5	0.86	2
			T=313.15 K			
2643	912.6	56.40	–929.9	148.4	0.79	8
			T=323.15 K			
3115	633.0	139.5	–1364	707.8	0.69	14
			T=333.15 K			
3646	–59.19	553.4	–2240	1460	0.49	21

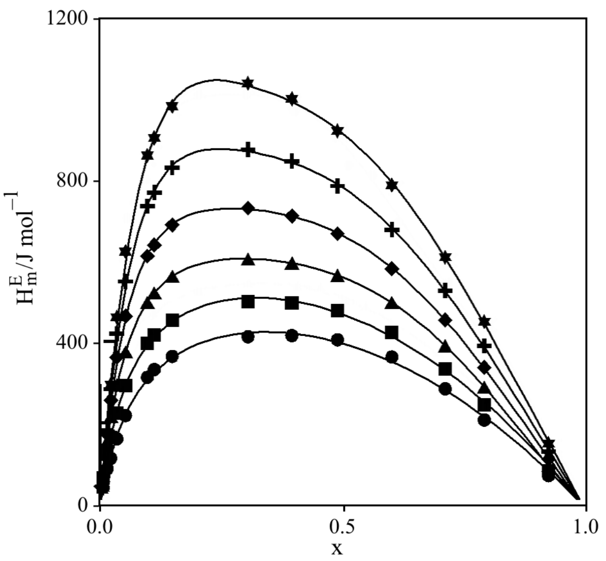

Fig. 3 Indirectly determined excess molar enthalpies H_m^E for x1-decanol+(1–x)n-decane at ● – T=283.15 K, ■ – T=293.15 K, ▲ – T=303.15 K, ◆ – T=313.15 K, ✚ – T=323.15 K, ✱ – T=333.15 K. — – Fitted values to Eq. (4)

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