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Excess enthalpies of mixtures of mono-carboxylic acid with dibutylether

Comparison with DISQUAC predictions

B. Marongiu · Silvia Porcedda · D. Falconieri · Alessandra Piras · E. Matteoli · L. Lepori

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Abstract In this article are reported the excess enthalpies, H^E, at 298.15 K, of liquid mixtures containing a linear mono-carboxylic acid (1) + di-*n*-butylether (2), determined by means of a titration calorimetric method. The experimental results, together with the literature data on thermodynamic properties of the above mentioned class of mixtures, have been interpreted in terms of the DISQUAC group contribution model. A set of structure-dependent interaction parameters, for the carboxylic group/oxygen contact, has been obtained. The model provides a fairly consistent description of the excess Gibbs energy, G^E and excess enthalpy, H^E, curves of the investigated mixtures.

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B. Marongiu (✉) · S. Porcedda · D. Falconieri · A. Piras
Dipartimento di Scienze Chimiche, Università degli Studi di Cagliari, Cittadella Universitaria, S.P. Monserrato—Sestu, km 0.700, 09042 Monserrato, CA, Italy
e-mail: maronb@unica.it

S. Porcedda
e-mail: porcedda@unica.it

D. Falconieri
e-mail: danilo.falconieri@tiscali.it

A. Piras
e-mail: apiras@unica.it

E. Matteoli · L. Lepori
CNR, Istituto per i Processi Chimico Fisici, via Moruzzi 1, 56124 Pisa, Italy
e-mail: matteoli@ipcf.cnr.it

L. Lepori
e-mail: lepori@ipcf.cnr.it

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Introduction

Group contribution models have been introduced to predict thermodynamic properties of binary mixtures. Accurate calculations, at present, are not possible without the use of experimental data concerning at least a small number of mixtures. Because of the characteristics of the liquid model adopted, these studies have been chiefly limited to classes of organic compounds. The studies developed around such models have greatly contributed to extend and correlate the mixing properties data banks.

DISQUAC [1, 2], a group contribution model developed on the basis of the Guggenheim's rigid lattice theory [3], calculates the excess thermodynamics properties as a sum of two contributions: one, DIS, due to dispersive forces, always present, whatever the kind of molecules and another, QUAC, depending on specific chemical interactions and steric effects.

Following a coherent strategy, in the application of the model we firstly examined mixtures of organic compounds of different polarity with linear and cyclic alkanes. Then, mixtures containing the same classes previously studied with a different second component having a moderate polarizability such as benzene and tetrachloromethane or other chemicals with similar polarizability [4–8].

Carboxylic acids are organic compounds that find application in different fields. They are characterized by a moderate polarity, practically independent of the length of the alkyl chain; dipolar moments measured in benzene at 303 K, of ethanoic, propanoic, and butanoic acid, are 1.68, 1.68, and 1.65 D, respectively [9]. The dissociation constant of all

carboxylic acids is of the order of 1×10^{-5}. Ethanoic acid is an excellent solvent for many organic compounds. Indeed, it is totally soluble in polar compounds such as water, ethanol, glycerol, diethyl ether, and in a polarisable substance-like carbon tetrachloride. It is instead practically insoluble in the apolar carbon disulfide [9].

In the past years, mixtures containing linear carboxylic acid with different organic solvent have been investigated to determine the thermodynamic mixing properties. In the open literature [10], the results can be found of the application of the DISQUAC model on mono-carboxylic acid mixtures with the following compounds: linear alkanes, cyclohexane, benzene, and tetrachloromethane.

In this study, we report the results of the experimental determination of the H^E at 298.15 K for mixtures containing a linear mono-carboxylic acid of general formula: CH_3–$(CH_2)_{p\text{-}2}$–CO_2H ($p = 2, 3, 4, 5, 6$) + di-*n*-butylether (DBE), CH_3–$(CH_2)_3$–O–$(CH_2)_3$–CH_3. Data used in the model application deal with vapor liquid equilibrium and correlated excess Gibbs energies, G^E and excess enthalpies, H^E.

Experimental

Materials

All organic chemicals were high purity reagents purchased from Sigma-Aldrich and were used without further purification. Their properties and fundamental constants, taken from literature [4], used in this study are collected in Table 1. Their purity was checked by gas chromatography, and their water content by Karl-Fischer analysis. No significant difference was found with respect to the impurity content declared by the factories.

As illustrated in previous works on V^E [11, 12], and H^E [13, 14], purity of substances is not a crucial requirement in excess properties measurements. We found that when the impurities are chemically similar to the substance they contaminate, as is usually the case, the value of the systematic error caused in the excess property is less than the impurity content %. The same holds for errors in the heats of solution, as confirmed in a previous work [15], by the close similarity of two sets of V^E and H^E results obtained using two samples of the same substance coming from two different factories and characterized by different purity degrees.

Table 1 Molar masses, purities express as mass fraction, densities at 298.15 K of chemicals used in the experiments

Compound	M/g mol^{-1}	Purity	ρ_{lit}/kg m^{-3}[a]
Ethanoic acid	60.052	0.997	1043.92
Propanoic acid	74.078	0.995	988.08
n-Butanoic acid	88.105	0.99	953.2
n-Pentanoic acid	102.131	0.99	934.5
n-Hexanoic acid	116.158	0.995	923.0
di-*n*-Butylether	130.228	0.993	764.1

[a] Taken from ref. [9]

Calorimetric measurements and data treatment

Heats of solution were collected through a heat flow calorimeter (Thermal Activity Monitor Mod. 2277) from Thermometric, Sweden. Experiments were conducted by adding a pure component, via Hamilton gas-tight syringes of capacity ranging from 100.0 to 1000 µL driven by Lund Syringe Pumps Mod. 6120, to an ampoule of 20 or 4 cm^3 capacity, initially charged with the other component or with a stock mixture of them. With this system, we were able to make accurate injections starting from a minimum of 1 µL, with precision 0.5%, and to measure accurate heat effects as small as 0.01 J, with sensitivity 0.5 µW. We chose this technique instead of mixing-flow calorimetry to avoid errors due to incomplete mixing and to obtain more precise values of the partial molar enthalpy at infinite dilution, useful in solvation studies.

The experimental solution heats, Q_{exp}, released by the additions of very small quantities of moles n of the titrant component j, n_j, are related to partial molar enthalpies, $\bar{H}_j$, by the equation: $\bar{H}_j \cong Q/n_j$. Calculated values of the solution heats, Q_{calc}, can be obtained by proper differentiation of the equation $H^E = f(x)$, x being the mole fraction, such as the Redlich–Kister (RK) one,

$$H^E = x_1 x_2 \sum_{k=1}^{n} c_k (x_1 - x_2)^{k-1} \Big/ (1 + c_0(x_1 - x_2)) \qquad (1)$$

A standard least squares procedure identifies the best values of c_k parameters at the minimum of the objective function $OF = \Sigma \left(Q_{exp} - Q_{calc}\right)^2$; they are reported in Table 2. Proper allowance was made for the heat involved in the phase composition changes brought about by the vapor–liquid equilibration after each addition. An exhaustive description of the apparatus, the experimental procedure, and the data treatment, can be found in previous articles [13, 16].

The uncertainty in the observed heat, Q, as determined by the reproducibility of the experiments and by integration of the peak area, can be evaluated as 0.5%. From σ's of c_k parameters (not reported in Table 2) we have calculated the standard deviations on H^E at equimolar mixtures, which range from ±0.7 to ±2.7 J mol^{-1}.

Results

As explained in previous articles [13, 16], the calorimetric experimental procedure generates a large amount of

experimental data ($\approx$396 experimental points in this case), which are not worth an extensive tabulation herein. These data can be retrieved as supplementary electronic material (DOC-file) or can be obtained from the Authors.

An example of how our experimental enthalpy data look like is given in Fig. 1, where the mixture propanoic acid + DBE is shown. The values of H^E at equimolar composition, of the partial molar enthalpies at infinite dilution, $\bar{H}_j^{\infty}$, together with other relevant literature data, are reported in Table 3. The molar excess Gibbs energies, G^E, have been obtained by reduction with the two or three parameters Redlich–Kister equation of the direct experimental isothermal P, x or P, x, y data [17]. Vapor phase imperfection was accounted for in terms of the second virial coefficient estimated by the Hayden and O'Connell [18] method.

Plots of H^E for all the mixtures here investigated are instead shown in Fig. 2. All measured systems are endothermic and the deviation from the ideal behavior is quite weak. Indeed, H^E values at equimolar composition are in the range [+390 ÷ +90] J mol^{-1} decreasing as the chain length of the acids increases.

To our knowledge, previous H^E or $\bar{H}_j$ data regarding the mixtures under examination are absent and only one reference on vapor–liquid equilibrium data for ethanoic or propanoic acid + di-*n*-butylether mixtures was found in the literature [17]. However, some data on excess enthalpies of similar systems can be found and are used here for comparison. They show that linear aliphatic acids exhibit a greater affinity toward di-butylether than toward linear and cyclic alkanes. Indeed, the acids here considered, when mixed with *n*-heptane [19, 20], give rise to endothermic effects having at equimolar composition values in the range [+936 ÷ +303] J mol^{-1}. Endothermic effect in the corresponding mixtures with cyclohexane are higher and in both cases, curves are quite symmetric with respect to the composition expressed as mole fraction. These experimental results, as expected, confirms the hypothesis that O atoms in the ether molecules exert attractive interactions with the carboxylic groups which are stronger than with aliphatic chains.

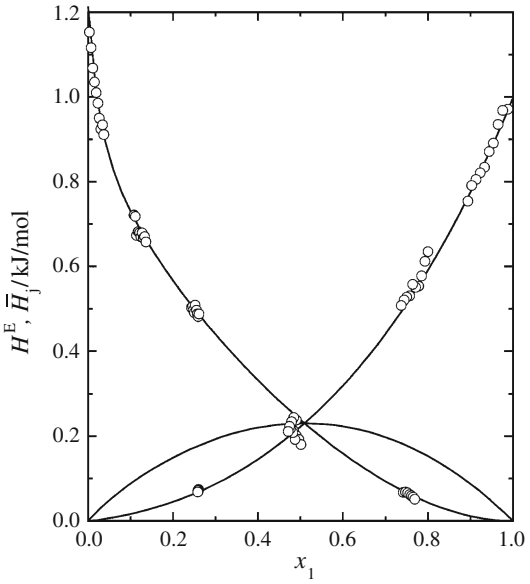

Fig. 1 Experimental partial molar enthalpies, $\bar{H}_1$ and $\bar{H}_2$, and excess enthalpies, H^E, of propanoic acid (1) + dibutylether (2) mixture versus x_1, the mole fraction of component 1

Theory

The class of mixtures under examination: linear carboxylic acid + dibutylether is regarded as possessing three types of contact surfaces among the following: type a, aliphatic (CH_3 and CH_2 groups in acids and dibutylether), type x, carboxylic group (COOH in acids) and type e, oxygen group in dibutylether. The equations used to calculate G^E and H^E in terms of DISQUAC are the same as in other applications [1, 2] and are not reported here.

The dispersive and the quasi-chemical interchange coefficients, concerning a contact among two different type of surfaces, $C_{uv,l}^{dis}$ and $C_{uv,l}^{quac}$ where {u, v} = {a, x, e} and $l = 1$ (Gibbs energy) or $l = 2$ (enthalpy) express the strength of interaction among the involved groups. Dispersive coefficients take into account physical cohesive forces meanwhile quasi-chemical coefficients are related to specific chemical interactions. Heat capacity coefficients, $l = 3$, are not considered.

Table 2 Values of the coefficients, c_i, of Eq. 1 and standard deviation of the fit, σ, for linear carboxylic acid (1) + di-*n*-butylether (2) mixtures

Component (1)	c_0	c_1/J/mol	c_2/J/mol	c_3/J/mol	c_4/J/mol	σ fit/MJ/mol
Ethanoic acid	0.90579	1562.39	1521.95	51.36	−79.90	12.0
Propanoic acid	0.90133	921.76	863.43	86.49	25.13	5.3
n-Butanoic acid	0.83339	558.25	395.30	−4.61	–	8.2
n-Pentanoic acid	0.84794	384.15	233.37	48.01	82.66	12.9
n-Hexanoic acid	0.70529	347.37	271.64	26.55	−90.15	3.6

Table 3 Molar excess Gibbs energies, G^E, molar excess enthalpies, H^E, at equimolar composition, partial molar enthalpies at infinite dilution, $\bar{H}_j^\infty$, of carboxylic acid (1) + di-*n*-butylether (2) mixtures: comparison of direct experimental results (exp) with values calculated (calc) using the coefficients $C_{uv,l}^{dis}$ and $C_{uv,l}^{quac}$ taken from literature [10, 22] and from Table 6

Component (1)	*T*/K	F^E (T, $x_1 = 0.5$)/J/mol		Source	$\bar{H}_1^\infty$/J/mol		$\bar{H}_2^\infty$/J/mol		Source
		Calc	Exp		Calc	Exp	Calc	Exp	
$F^E = G^E$									
Ethanoic acid	298.15	415							
	343.15	420	420[a]	[17]					
Propanoic acid	298.15	463							
	343.15	499	499[a]	[17]					
$F^E = H^E$									
Ethanoic acid	298.15	391	391 ± 2.0	[Ts][b]	1480	1823	2186	1603	[Ts]
Propanoic acid	298.15	231	230 ± 1.1	[Ts]	1020	1213	1003	998	[Ts]
Butanoic acid	298.15	140	140 ± 1.1	[Ts]	923	950	490	518	[Ts]
Pentanoic acid	298.15	100	96 ± 2.7	[Ts]	570	764	310	405	[Ts]
Hexanoic acid	298.15	83	87 ± 0.7	[Ts]	493	653	253	326	[Ts]

[a] Calculated (this study) by reduction of the original *P*, *x* or *P*, *x*, *y* data with the 2- or 3-parameters Redlich–Kister equation, vapor phase non-ideality corrected in terms of the second virial coefficient

[b] [Ts] means this study

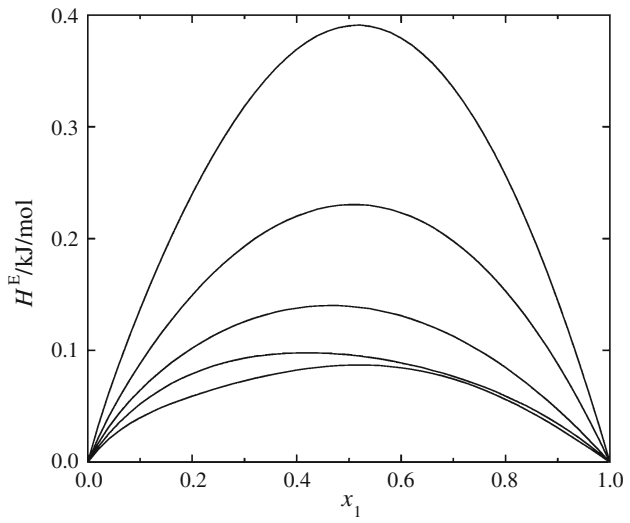

Fig. 2 Excess enthalpies, H^E, at 298.15 K, for carboxylic acid (1) + dibutylether (2) mixtures versus x_1, the mole fraction of component (1) calculated from Eq. 1 with parameters of Table 2; from top to bottom: ethanoic acid, propanoic acid, butanoic acid, pentanoic acid, hexanoic acid

Assessment of geometrical parameters

The relative geometrical parameters as volumes, r_i, surfaces, q_i, and, molecular surface fractions α_{vi}, of all the molecular species have been calculated on the basis of the relative group parameters, the volumes, r_G, and surfaces, q_G, taking arbitrarily the volume, V_{CH_4}, and surface, A_{CH_4}, of methane as unity. Thus, $r_G = V_G/V_{CH_4}$ and $q_G = A_G/A_{CH_4}$. In general, the V_G and A_G values calculated by Bondi [21], have been adopted.

The relative group parameters used in this study are reported in Table 4. Table 5 lists the geometrical parameters of all compounds referred to in this article.

Estimation of interaction parameters

The groups investigated in this study are non-polar (type a), polarisable (type e), or polar (type x). To improve the prediction, in the application of the model, we make the assumption that the parameters may vary with the molecular structure, in particular for the first members of homologous series. The variation should be regular and similar classes should follow the same rules. The final selection of parameters is achieved by plotting the, usually few, adjusted values on smooth curves and estimating the other values by interpolation or extrapolation.

Mixtures under examination are characterized by three types of contacts; (a, x), (a, e), and (e, x). In this study, we adopted the interchange parameters found in the literature for the (a, e) and (a, x) contacts and report the values determined for the (e, x)-contact. The rules we found are as follows:

(i) (a, e)-contact. The DISQUAC treatment on linear oxaalkane + hydrocarbon mixtures is reported in literature [22]. The dispersive coefficients are the same for all non-cyclic mono-ethers and polyethers: $C_{ae,1}^{dis} = 10.6$, $C_{ae,2}^{dis} = 18.2$. The quasichemical coefficients of linear mono-ethers decrease with increase in the chain length of the oxygenated compound but are independent from the length of *n*-alkane. As a consequence all systems considered in this article, containing DBE as second component, are characterized by identical values for each (a, e) contact: $C_{ae,1}^{quac} = 2.6$ and $C_{ae,2}^{quac} = 1.5$.

Table 4 Relative group increments for molecular volumes, $r_G = V_G/V_{CH_4}$, and areas, $q_G = A_G/A_{CH_4}$, calculated by Bondi's method [21], ($V_{CH_4} = 17.12 \times 10^{-6}$ m^3 mol^{-1}, $A_{CH_4} = 2.90 \times 10^5$ m^2 mol^{-1})

Group	r_G	q_G
–CH_3	0.79848	0.73103
–CH_2–	0.59755	0.46552
–COOH	1.15304	1.05517
–O–	0.21612	0.20690

Table 5 Relative volumes, r_i, relative total surfaces, q_i, and molecular surface fractions, α_{vi}, (v = a, x, e) calculated from the group increments r_G and q_G given in Table 4; a (CH_3, CH_2); x (COOH); e (O)

Compound	r_i	q_i	α_{ai}	α_{xi}	α_{ei}
Ethanoic acid	1.9515	1.7862	0.4093	0.5907	0.0000
Propanoic acid	2.5491	2.2517	0.5314	0.4686	0.0000
n-Butanoic acid	3.1466	2.7172	0.6117	0.3883	0.0000
n-Pentanoic acid	3.7442	3.1828	0.6685	0.3315	0.0000
n-Hexanoic acid	4.3417	3.6483	0.7108	0.2892	0.0000
di-*n*-Butylether	5.3984	4.4621	0.9536	0.0000	0.0463

(ii) (a, x)-contact. The interchange coefficients calculated from thermodynamic properties of carboxylic acid + *n*-alkane mixtures have been adopted [10]. The Gibbs energy dispersive coefficients of the (a, x)-contact, $C^{dis}_{ax,1}$, are negative and decrease with increasing p, the number of methylene groups in the carboxylic acid (from 2 to 4) and remain constant for p $\geq$ 4. The values are in the range [$-0.40 \div -0.85$]. The corresponding enthalpic coefficients, $C^{dis}_{ax,2}$, vary in the range [$0.30 \div 0.70$] for carboxylic acids having from 2 to 6 carbon atoms. The third coefficient is constant: $C^{dis}_{ax,3} = 5.00$ for every system. The quasi-chemical coefficients are constant: $C^{quac}_{ax,1} = 4.00$, $C^{quac}_{ax,2} = 1.50$ and $C^{quac}_{ax,3} = -10.00$. Both dispersive and quasi-chemical heat capacity coefficients have been ignored, as it has been done in most DISQUAC treatment.

(iii) (e, x)-contact. All coefficients values concerning this contact are collected in Table 6. Because of the scarcity of Gibbs energy data, it has been possible to calculate only the first two terms of the dispersive coefficients, $C^{dis}_{ex,1}$. Their values are -4.42 for the ethanoic acid and 1.13 for propanoic acid. The values of the enthalpic dispersive parameters, $C^{dis}_{ex,2}$, are comprise between 13.55 for ethanoic acid and 9.92 for hexanoic acid. The quasi-chemical coefficients, $C^{quac}_{ex,1} = -0.30$ and $C^{quac}_{ex,2} = -0.60$ are negative and independent of the chain length of the *n*-alkyl groups adjacent to the carboxylic group.

Table 6 Dispersive and quasi-chemical interchange energy coefficients for contact (e, x) in linear carboxylic acid (1) + di-*n*-butylether (2) mixtures; p represents the total number of C atoms in the carboxylic acid

p	$C^{dis}_{ex,1}$	$C^{dis}_{ex,2}$	$C^{quac}_{ex,1}$	$C^{quac}_{ex,2}$
2	−4.42	14.05	−0.30	−0.60
3	1.13	11.75	−0.30	−0.60
4	1.13[a]	10.37	−0.30[a]	−0.60
≥5	1.13[a]	9.92	−0.30[a]	−0.60

[a] Guessed value

Comparison with experiment and discussion

Sometimes polar/polar or polar/polarisable groups contacts are correctly described by an entirely dispersive approach [23, 24]. This is possible when intermolecular forces exerted by the two different groups are similar. In the case of mixtures under investigation: R–CO_2H + C_4H_{11}–O–C_4H_{11}, as in other cases [25, 26], it has been necessary to consider also a quasi-chemical contribution.

Because of the scarcity of G^E data, the agreement between experimental and calculated values will not be discussed. The comparison between experimental and DISQUAC results on H^E data concerning carboxylic acid + DBE mixture is shown in Fig. 3. In Table 3 are compared also the values concerning excess enthalpies at infinite dilution. The model calculates, to a different extent, higher values for $\bar{H}_2^\infty$and lower values for $\bar{H}_1^\infty$. Altogether, the experimental-calculated agreement on H^E is quite satisfactory.

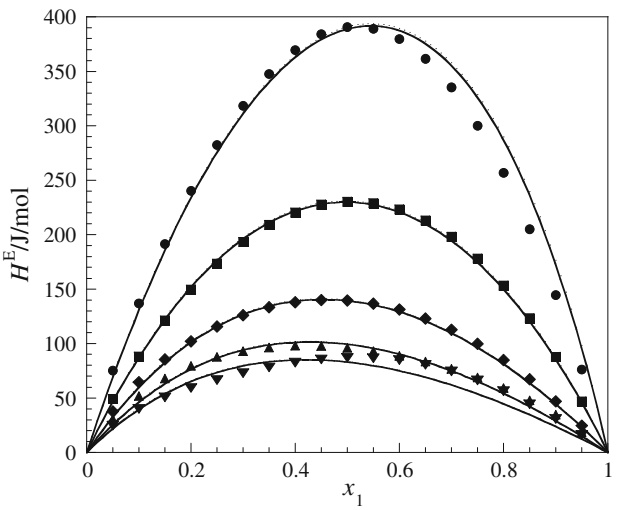

Fig. 3 Comparison of theory with experiments for the molar excess enthalpies, H^E, at 298.15 K, for carboxylic acid (1) + dibutylether (2) mixtures versus x_1, the mole fraction of component (1): full lines, DISQUAC predictions; points, experimental results, this study: *filled circle* ethanoic acid, *filled square* propanoic acid, *filled diamond* butanoic acid, *filled triangle* pentanoic acid, *filled inverted triangle* hexanoic acid

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