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Thermodynamics of (ketone + amine) mixtures. Part XI. Excess molar enthalpies at $T = 298.15$ K for the (1-propanol + *N,N,N*-triethylamine + 2-butanone) system

Iván Alonso, Juan Antonio González *, Isaías García De La Fuente, José Carlos Cobos

G.E.T.E.F., Departamento de Física Aplicada, Facultad de Ciencias, Universidad de Valladolid, Paseo de Belén, 7, 47011 Valladolid, Spain

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ABSTRACT

Molar excess enthalpies, H^E_m, measured by means of a Tian-Calvet microcalorimeter, for the ternary system {1-propanol + *N,N,N*-triethylamine (TEA) + 2-butanone} at $T = 298.15$ K are reported. Values of H^E_m for the constituent binaries are available in the literature. The data are interpreted in terms of different interactional contributions to H^E_m. The coefficients of the corresponding fittings of binary and ternary H^E_m values have been used to determine the partial molar excess enthalpies of each component. It is concluded that 1-propanol and TEA molecules can participate in interactions between unlike molecules, and that 2-butanone is mainly a breaker of interactions between like molecules. The DISQUAC model is applied, using binary parameters only, for the H^E_m prediction of the ternary mixture investigated. Large differences between experimental values and theoretical results show the existence of ternary interactions.

1. Introduction

Amides, aminoacids, peptides and their derivatives, as proteins, which are polymers linked to each other by peptide bonds, are very important compounds in biochemistry. On the other hand, aqueous solutions of *N,N*-dimethylformamide or *N*-methylformamide can be considered as a solvent representing the interior of proteins. Hence, the investigation of systems containing the carbonyl and/or the amine groups in the same or in different molecules, and of mixtures containing these groups and short chain 1-alkanols is a necessary first step for a better understanding of the structure and interactions present in solutions of biological interest. For this reason, we are involved in a systematic research of (amine + alkanone) mixtures and of amide systems. Thus, we have reported volumetric and calorimetric data for (aniline, or *N*-methylaniline, or dipropylamine, or dibutylamine, or TEA + 2-alkanone systems) [1–10], and liquid–liquid equilibria measurements for (*N,N*-dialkylamide, or ε-caprolactam + alkane) mixtures [11–13]. The DISQUAC [14] and ERAS [15] models have been used for the study of (amine + 2-alkanone) mixtures [9,10], and of solutions containing *N,N*-dialkylamide [16], or *N*-alkylamide [17,18] or *N*-methylpyrrolidone [19], or ε-caprolactam [12] and different solvents (*e.g.* as alkanes or 1-alkanols). The formalism of the Kirkwood–Buff integrals [20] have been also applied to gain insight into the structure of (*N,N*-dialkylamide + 1-alkanol systems) [16]. As continuation of this research, we report now H^E_m data at $T = 298.15$ K and atmospheric pressure for the {1-propanol + TEA + 2-butanone} mixture.

2. Experimental

2.1. Materials

Table 1 shows information on source, purity and density, ρ, of the pure compounds. The chemicals were used without further purification. Densities were measured using a vibrating-tube densimeter and a sound analyser, Anton Paar model DSA-5000. The uncertainty for the ρ values is $(1 \times 10^{-2}$ kg · m^{-3}, while the corresponding precision is $(1 \times 10^{-3}$kg · m^{-3}. The ρ values of the pure liquids are in good agreement with those from the literature (table 1).

2.2. Apparatus and procedure

Binary mixtures were prepared by mass, using an analytical balance HR-202 (weighing accuracy ± 0.01 kg), with all weighing corrected for buoyancy effects. The error on the final mole fraction is estimated to be lower than ±0.0006 (the relative error lower than 0.1%). Molar quantities were calculated using the relative atomic mass table of 2006 issued by IUPAC [21].

* Corresponding author. Tel.: +34 983 423757; fax: +34 983 423136.
E-mail address: jagl@termo.uva.es (J.A. González).

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TABLE 1
Source, purity and densities, ρ, of pure compounds at $T = 298.15$ K and atmospheric pressure. Comparison of experimental (Exp.) ρ[a] values with those from the literature (Lit.).

Compound	Source	Mass fraction purity[b]	ρ/cm^3 · mol^{-1}	
			Exp.	Lit.
1-Propanol	Fluka	⩾0.995	0.799656	0.79976[c]; 0.79965[d]
2-Butanone	Fluka	⩾0.995	0.799969	0.7997[e,f]; 0.79992[g]
N,*N*,*N*-triethylamine (TEA)	Sigma–Aldrich	⩾0.995	0.722814	0.72318[j]; 0.72376[k]

[a] Density uncertainty, $u(\rho) = 0.01$ kg · m^{-3}.
[b] In mass fraction.
[c] Reference [50].
[d] Reference [51].
[e] Reference [52].
[f] Reference [53].
[g] Reference [54].
[j] Reference [55].
[k] Reference [56].

TABLE 2
Excess molar enthalpies, H^E_m, for the ternary system {1-propanol(1) + TEA(2) + 2-butanone(3)} at differents x_2/x_3 ratios, $T = 298.15$ K and atmospheric pressure.[a].

x_1	H^E_m /J·mol^{-1}	x_1	H^E_m /J·mol^{-1}	x_1	H^E_m /J·mol^{-1}
$x_2/x_3 = 0.3264$ ($x_2' = 0.2461$, $x_3' = 0.7539$)		$x_2/x_3 = 1.0249$ ($x_2' = 0.5061$, $x_3' = 0.4939$)		$x_2/x_3 = 2.9529$ ($x_2' = 0.7470$, $x_3' = 0.2530$)	
0.0769	482	0.0691	521	0.0944	259
0.1301	458	0.1133	393	0.1453	38
0.1697	441	0.1672	255	0.1920	−133
0.2225	425	0.2211	124	0.2225	−230
0.2723	412	0.2653	22	0.2709	−371
0.3157	405	0.3111	−64	0.3094	−471
0.3598	399	0.3610	−140	0.3651	−626
0.4031	398	0.3971	−191	0.4057	−691
0.4547	393	0.4524	−279	0.4563	−771
0.5030	388	0.5031	−312	0.4996	−852
0.5479	380	0.5533	−345	0.5535	−897
0.5922	373	0.6027	−347	0.5963	−927
0.6467	359	0.6451	−377	0.6479	−909
0.6947	336	0.6960	−336	0.6997	−877
0.7399	313	0.7487	−310	0.7488	−813
0.7939	271	0.8002	−259	0.7911	−719
0.8313	239	0.8403	−228	0.8362	−619
0.8811	182	0.8914	−169	0.8872	−477
0.9332	107	0.9410	−105	0.9336	−313

[a] Uncertainties, u are; $u(x_1) = 0.0006$; $u(H^E_m) = (0.01 \cdot H^E_m)$ J · mol^{-1}.

TABLE 3
Coefficients A_i and standard deviations, $\sigma(H^E_m)$ (equation (5)) for representation of H^E_m at $T = 298.15$ K for the binaries involved in the {1-propanol(1) + TEA(2) + 2-butanone(3)} system by equation (3).

System	A_0	A_1	A_2	A_3	$\sigma(H^E_m)$/J · mol^{-1}
1-propanol + TEA [32]	−5700	−2230	398	−2100	12.5
1-propanol + 2-butanone [31]	5006	−213	778		1.4
TEA + 2-butanone [10]	2982	400	330	460	6

A standard Calvet-type microcalorimeter, equipped with a batch mixing cell with a small (<2%) gas phase, was used to determine H^E_m over the entire mol fraction range. Measurements were carried out at $T = 298.15$ K and atmospheric pressure. Details of the experimental technique can be found elsewhere [8,22]. The calorimeter was tested comparing our H^E_m measurements with those available in the literature for the systems (cyclohexane + benzene) and (cyclohexane + 2,2,4-trimethylpentane). Our results differ by less than 1% from those of the literature [23,24] near $x_1 = 0.5$.

Experimental measurements were carried out for the ternary compositions resulting from adding 1-propanol to the binary mixture {TEA (x_2') + 2-butanone (x_3')}, where $x_3' = 1 - x_2'$. The ternary system may be considered then a pseudobinary solution composed by 1-propanol (x_1) and that binary mixture (x_2). Thus, the excess molar enthalpy at the pseudobinary composition x_2, x_3, ($x_1 = 1 - x_2 - x_3$) can be expressed as:

$$H^E_m = H^E_{m,\psi} + (x_2 + x_3) \cdot H^E_{m,23'}, \quad (1)$$

TABLE 4
Coefficients B_i (equation (4)) and standard deviations, $\sigma(H^E_m)$ (equation (5)) for representation of H^E_m at $T = 298.15$ K for the ternary system {1-propanol(1) + TEA(2) + 2-butanone(3)} by equation (2).

B_0	B_1	B_2	B_3	B_4	$\sigma(H^E_m)$/J · mol^{-1}
−5.4	0.2	−8.0	3.0	6.4	14