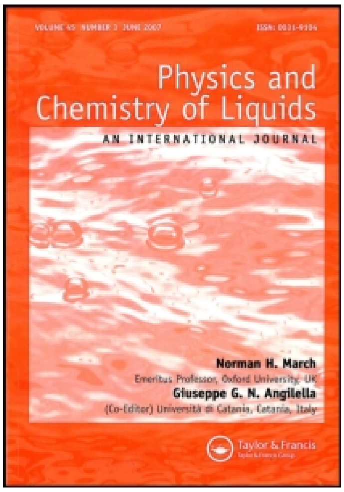

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Thermodynamics of mixtures containing a very strongly polar compound: IV - application of the DISQUAC, UNIFAC and ERAS models to DMSO+ organic solvent systems

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THERMODYNAMICS OF MIXTURES CONTAINING A VERY STRONGLY POLAR COMPOUND: IV – APPLICATION OF THE DISQUAC, UNIFAC AND ERAS MODELS TO DMSO + ORGANIC SOLVENT SYSTEMS

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Binary mixtures of dimethylsulfoxide (DMSO) with alkane, benzene, toluene 1-alkanol, or 1-alkyne have been investigated in terms of DISQUAC. The corresponding interaction parameters are reported. ERAS parameters for 1-alkanol + DMSO mixtures are also given. ERAS calculations were developed considering DMSO as a not self-associated compound.

DISQUAC represents fairly well a complete set of thermodynamic properties: molar excess enthalpies, molar excess Gibbs energies, vapor–liquid equilibria, natural logarithms of activity coefficients at infinite dilution, or partial molar excess enthalpies at infinite dilution. DISQUAC improves UNIFAC calculations for H^E. Both models yield similar results for VLE. In addition, DISQUAC also improves, ERAS results for 1-alkanol + DMSO mixtures. This may be due to ERAS cannot represent the strong dipole–dipole interactions present in such solutions.

Keywords: Thermodynamics; Mixtures; DMSO; 1-Alkanol; Models; Dipole–dipole interactions

1. INTRODUCTION

We are engaged in a systematic study of solutions containing a component with a very high dipolar moment in gas phase (μ), e.g., propylene carbonate ($\mu = 4.94$ D [1]), 1-methyl-2-pyrrolidinone (NMP; $\mu = 4.09$ D [1]), dimethyl sulfoxide (DMSO; $\mu = 4.06$ D [1]) or sulfolane ($\mu = 4.80$ D [1]).

In the previous works of this series, we have reported liquid–liquid and solid–liquid equilibria (LLE, SLE) for sulfolane + 1-alkanol mixtures [2], and SLE for sulfonate + nitrile systems [3]. In addition, solutions formed by sulfolane [2,3] or tertiary amide [4]

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and several organic solvents (alkane, benzene, toluene, CCl_4, 1-alkanol, nitrile or 1-alkyne) have been characterized in terms of DISQUAC [5,6], an extended group contribution model based on the rigid lattice theory developed by Guggenheim [7].

DMSO is an aprotic linear molecule [8]. In the pure liquid, DMSO has a cluster structure [9,10]. This structure is partially retained in the mixture [11]. So, H^E of the DMSO + CCl_4 system is an extremely unsymmetrical function of composition [8], suggesting strong self-association between DMSO molecules. The excess molar heat capacity at constant pressure (C_p^E) of the DMSO + benzene mixture is s-shaped [12]. This has been interpreted [13] by assuming that the clusters of DMSO in the pure state are left unbroken to some extent, even in the mixture, and that the smooth benzene molecules slip in to occupy the spaces among the clusters. The formation of the mentioned molecular structures is not produced by hydrogen bonding. It has been attributed to dipolar interactions between DMSO molecules [14–16], or to the presence in the liquid of strong but nonspecific dipole–dipole forces [17]. So, DMSO is not miscible with alkanes. However, the sulfoxide group can act as an electron donor in hydrogen-bonded complex formation. It is supported by the H^E values of DMSO + chloroform or + methanol mixtures. At equimolar composition and 298.15 K, they are, respectively, -2825 J mol [18–19] or -350 J mol^{-1} [20].

These properties make interesting the study of systems containing DMSO. In the present article, DMSO + alkane, + benzene or + toluene, + 1-alkanol or + 1-alkyne are studied in terms of DISQUAC [5,6]. The ERAS model [21], which combines the real association solution model [22–25] with the Flory equation of state [26] is also applied to 1-alkanol + DMSO mixtures. DMSO + 1-alkyne systems have been previously treated using ERAS [27], under the assumption that both compounds are self-associated, which is not strictly justified. Interaction parameters for some solutions containing DMSO are also available in the framework of the DORTMUND version of UNIFAC [28,29].

2. MODELS

2.1. DISQUAC

2.1.1. Assessment of Geometrical Parameters

When DISQUAC is applied, the total relative molecular volumes, r, surfaces, q, and the molecular surface fractions, α, of the compounds present in the mixture are usually calculated additively on the basis of the group volumes R_G and surfaces Q_G recommended by Bondi [30]. As volume and surface units, the volume R_{CH_4} and the surface Q_{CH_4} of methane are taken arbitrarily [31]. For the sulfoxide group, $r_{SO} = 0.90771$ and $q_{SO} = 0.66896$. The geometrical parameters for other groups referred to in this work are given elsewhere [31–33].

2.1.2. Equations

The equations used to calculate G^E and H^E are the same as in other applications [32]. The interactional terms in the excess thermodynamic properties G^E and H^E contain a DIS (dispersive) and a QUAC (quasichemical) contribution which are calculated independently by the classical formulas and then simply added. The degree of nonrandomness is thus expressed by the relative amounts of dispersive and quasichemical terms:

$$G^E = G^{E,\mathrm{COMB}} + G^{E,\mathrm{DIS}} + G^{E,\mathrm{QUAC}} \tag{1}$$

$$H^E = H^{E,\mathrm{DIS}} + H^{E,\mathrm{QUAC}} \tag{2}$$

where $G^{E,\mathrm{COMB}}$ is the Flory–Huggins combinatorial term [31,34]. For the QUAC part, the reference value $z = 4$ was chosen for the coordination number.

The temperature dependence of the interaction parameters g_{st}, h_{st} and c_{pst} (where s, t are two groups present in the solution, $\mathrm{s} \neq \mathrm{t}$) has been expressed in terms of the DIS and QUAC interchange coefficients $C^{\mathrm{DIS}}_{\mathrm{st},l}$ and $C^{\mathrm{QUAC}}_{\mathrm{st},l}$ ($l = 1$, Gibbs energy, $g^{\mathrm{DIS/QUAC}}_{\mathrm{st}}(T_o)/RT_o = C^{\mathrm{DIS/QUAC}}_{\mathrm{st},l}$; $l = 2$, enthalpy $h^{\mathrm{DIS/QUAC}}_{\mathrm{st}}(T_o)/RT_o = C^{\mathrm{DIS/QUAC}}_{\mathrm{st},2}$; $l = 3$, heat capacity, $c^{\mathrm{DIS/QUAC}}_{\mathrm{pst}}(T_0)/R = C^{\mathrm{DIS/QUAC}}_{\mathrm{st},3}$). T_o is the scaling temperature, 298.15 K. The mentioned temperature dependence is as follows:

$$\begin{aligned} g^{\mathrm{DIS/QUAC}}_{\mathrm{st}}/RT = C^{\mathrm{DIS/QUAC}}_{\mathrm{st},1} &+ C^{\mathrm{DIS/QUAC}}_{\mathrm{st},2}[(T_o/T) - 1] \\ &+ C^{\mathrm{DIS/QUAC}}_{\mathrm{st},3}[\ln(T_o/T) - (T_o/T) + 1] \end{aligned} \tag{3}$$

$$h^{\mathrm{DIS/QUAC}}_{\mathrm{st}}/RT = C^{\mathrm{DIS/QUAC}}_{\mathrm{st},2}(T_o/T) - C^{\mathrm{DIS/QUAC}}_{\mathrm{st},3}[(T_o/T) - 1] \tag{4}$$

$$c^{\mathrm{DIS/QUAC}}_{\mathrm{pst}}/R = C^{\mathrm{DIS/QUAC}}_{\mathrm{st},3} \tag{5}$$

Due to DMSO + alkane mixtures show miscibility gaps, it is necessary to calculate the LLE coexistence curves. This was done by taking into account that the values of x_1 (x'_1, x'_2) relating to the two phases in equilibrium are such that the functions $G^{M'}$ and $G^{M''}$ ($G^M = G^{E'} + G^{\mathrm{ideal}}$) have a common tangent [35–37].

2.2. Modified UNIFAC (Dortmund Version)

The modified UNIFAC model [28,29] differs from the original UNIFAC [38] by the combinatorial term and the temperature dependence of the group interaction parameters.

The equations used to calculate G^E and H^E are obtained from the fundamental equation for the activity coefficient γ_i of component *i*:

$$\ln \gamma_i = \ln \gamma_i^{\mathrm{COMB}} + \ln \gamma_i^{\mathrm{RES}} \tag{6}$$

where $\ln \gamma_i^{\mathrm{COMB}}$ is the combinatorial term and $\ln \gamma_i^{\mathrm{RES}}$ is the residual term. Equations are given elsewhere [28].

2.2.1. Assessment of Geometrical and Interaction Parameters

In modified UNIFAC, alkanols are characterized by two main groups, OH and CH_3OH. The former is subdivided into three subgroups: OH(p); OH(s) and OH(t), which represent the hydroxyl group in primary, secondary and tertiary alcohols. CH_3OH is a group itself which characterizes methanol. DMSO is also a main group itself. Benzene is considered a homogeneous molecule, while there are two main groups in toluene. The subgroups have different geometrical parameters, but the subgroups within the same main group are assumed to have identical group energy-interaction parameters.

The geometrical parameters, the relative van der Waals volumes and the relative van der Waals surfaces of the different subgroups are not calculated from molecular parameters like in the original UNIFAC, but are obtained together with the interaction parameters by fitting equations to the experimental values of the thermodynamic properties considered. The geometrical and interaction parameters are taken, when available, from the literature [28,29] and are used without modification.

2.3. The ERAS Model

This model combines the real association solution model [22–25] with Flory equation of state [26]. The excess functions are written as

$$X^E = X^E_{\text{phys}} + X^E_{\text{chem}} \tag{7}$$

where $X = G$ (Gibbs energy), H (enthalpy), V (volume). In Eq. (7), X_{chem} is the chemical contribution, and arises from chemical interactions between the molecules, in particular hydrogen bonding. X_{phys} represents the physical contribution, consequence of the physical interactions between molecules. Expressions for these terms when cross-association between compounds exist are given elsewhere [39–41] for $X = H$ and V, and will not be repeated here. In this work, calculations are developed assuming that DMSO is not self-associated, but that cross-association exists in systems of 1-alkanol with DMSO.

Hydrogen bonding is characterized by self-association constants, K_A, hydrogen bonding energies, Δh^*_A, and reaction volumes of hydrogen bonding, Δv^*_A for self-association of component A (1-alkanol). Similarly, cross-association between components is characterized by K_{AB}, Δh^*_{AB}, Δv^*_{AB}.

X_{phys} is derived from Flory equation of state [26], which is assumed to be valid not only for pure components but also for the mixtures. The reduction parameters for pure components, hard core volume of the molecules, V^*, intermolecular energy density P^* and temperature reduction parameter (T^*), required to calculate the reduced parameters $\bar{P}_i = P/P^*_i$; $\bar{V}_i = V_i/V^*_i$ and $\bar{T}_i = T/T^*_i$ which appear in the equation of state, are obtained from previous determination of density, thermal expansion coefficient and compressibility which can be obtained from experimental P–V–T data. They also depend on K_A, Δh^*_A, Δv^*_A. Details of the calculations are described elsewhere [40–41].

The reduction parameters for the mixture (P^*_M and V^*_M) are calculated via mixing rules [41–42]), where X_{AB}, the energetic interaction parameter characterizing the difference of dispersive intermolecular interactions between molecules A and B in the solution and in the pure components is introduced. It is the only adjustable parameter of the physical part of H^E and V^E.

The geometrical parameters of the molecule were calculated, as in DISQUAC, using Bondi's method [30].

3. ESTIMATION OF MODEL PARAMETERS

3.1. DISQUAC

In terms of DISQUAC, DMSO + n-alkane solutions are regarded as possessing two types of surfaces: (i) type a, aliphatic, CH_3 and CH_2 in n-alkanes (which is also present in toluene, DMSO, 1-alkanols or 1-alkynes); (ii) type d, SO in DMSO. Mixtures including cycloalkane, benzene or toluene, 1-alkanol or 1-alkyne have a third type of surface, type s, s = c, cyclic, c-CH_2 in cycloalkanes; s = b, C_6H_6 in benzene; s = p, C_6H_5 in toluene; s = h, hydroxyl, OH in 1-alkanols; s = y, HC≡C in 1-alkynes.

The general procedure for estimating the model parameters has been explained in detail in the first article of this series [2] and will not be repeated. Some remarks are given below.

3.1.1. DMSO + n-Alkane

These systems are characterized by one contact (a, d). So, the fitting of the interaction parameters is rather straightforward. Due to the lack of data on G^E and H^E, the $C_{\mathrm{ad},l}^{\mathrm{DIS/QUAC}}$ (l = 1,2,3) coefficients were determined using the available data in the literature on $\ln \gamma_i^\infty$ (natural logarithms of activity coefficients at infinite dilution) and $H_i^{E,\infty}$ (partial molar excess enthalpies at infinite dilution). Final parameters are given in Table I.

3.1.2. DMSO + Cycloalkane

Here, three types of contacts exist: (a, c); (a, d) and (d, c). The interaction parameters for the (a, c) contacts were neglected [2,4]. The $C_{\mathrm{ad},l}^{\mathrm{DIS/QUAC}}$ coefficients are known. Those for the (c, d) contacts were calculated (Table I), using $\ln \gamma_i^\infty$ and $H_i^{E,\infty}$ data for the present solutions, under the basic assumption that the systems with n-alkane or cycloalkane are characterized by the same QUAC parameters, and different DIS parameters. This rule has been observed to be valid for many other mixtures,

TABLE I Interchange coefficients, dispersive $C_{\mathrm{ds},l}^{\mathrm{DIS}}$, and quasichemical $C_{\mathrm{ds},l}^{\mathrm{QUAC}}$ (l = 1, Gibbs energy; l = 2, enthalpy, l = 3, heat capacity) for contacts (d, s)[a] present in DMSO + organic solvent mixtures

Solvent	*Contact (d, s)*	$C_{ds,1}^{\mathrm{DIS}}$	$C_{ds,2}^{\mathrm{DIS}}$	$C_{ds,3}^{\mathrm{DIS}}$	$C_{ds,1}^{\mathrm{QUAC}}$	$C_{ds,2}^{\mathrm{QUAC}}$	$C_{ds,3}^{\mathrm{QUAC}}$
n-Alkane	(d, a)	8.7	14.0		6.0	4.0	
Cycloalkane	(d, c)	9.2	14.5		6.0	4.0	
Benzene	(d, b)	12.13	10.90	8.7	−1.3	0.2	−4.5
Toluene	(d, p)	12.00	10.55	8.7	−1.3	0.2	−4.5
Methanol	(d, h)	0.5	8.5	6.0	−1.6	−2.65	4.0
Ethanol	(d, h)	1.1	8.5	6.0	−1.6	−1.35	4.0
1-Propanol	(d, h)	1.1	0.86	6.0	−1.6	0.75	4.0
1-Butanol	(d, h)	1.1	−0.4	6.0	−1.6	0.75	4.0
1-Pentanol	(d, h)	1.1	−1.4	6.0	−1.6	0.75	4.0
1-Hexanol	(d, h)	1.1	−4.5	6.0	−1.6	0.75	4.0
1-Pentyne	(d, y)	−1.65	1.1	6.0	10.0	−20.0	
1-Heptyne	(d, y)	−1.65	0.2		10.0	−20.0	
≥ (1-Octyne)	(d, y)	−1.65	−1.1		10.0	−20.0	

[a] d, SO in DMSO; $s = a$, CH_3, CH_2 in n-alkanes, toluene, DMSO, 1-alkanols or 1 = alkynes; s = b, C_6H_6; s = c, c-CH_2 in cycloalkanes; s = h, OH in 1-alkanols; s = p, C_6H_5 in toluene; s = y, HC≡C in 1-alkynes.

e.g. oxaalkane [43], chloroalkane [44], *n*-alkanone [45], linear organic carbonate [46], sulfolane [2], tertiary amide [4] or alkanol [47–50] + *n*-alkane, or + cyclohexane.

3.1.3. DMSO + Benzene, or + Toluene

These systems are characterized by three types of contacts (a, d), (a, s) and (d, s) with s = b or p. The (a, s) contacts (s = b, p) are entirely dispersive [51]. The values used are $C^{\mathrm{DIS}}_{\mathrm{ab},1} = 0.289$; $C^{\mathrm{DIS}}_{\mathrm{ab},2} = 0.565$; $C^{\mathrm{DIS}}_{\mathrm{ab},3} = -0.585$; $C^{\mathrm{DIS}}_{\mathrm{ap},1} = 0.390$; $C^{\mathrm{DIS}}_{\mathrm{ap},2} = 0.590$; $C^{\mathrm{DIS}}_{\mathrm{ap},3} = -0.350$. The estimation of the $C^{\mathrm{DIS/QUAC}}_{\mathrm{ds},l}$ ($l = 1, 2, 3$) coefficients was developed assuming that the $C^{\mathrm{QUAC}}_{\mathrm{ds},l}$ coefficients are independent of the aromatic compound. The same assumptions was applied, e.g., for sulfolane [2], tertiary amide [4] or 1-alkanol [52] + benzene, or + toluene. The final $C^{\mathrm{DIS/QUAC}}_{\mathrm{ds},l}$ ($l = 1, 2, 3$) coefficients are collected in Table I.

3.1.4. 1-Alkanol + DMSO

The contacts present in these solutions are: (a, d), (a, h) and (d, h). The (a, h) contacts are represented by DIS and QUAC interchange coefficients obtained from experimental data for 1-alkanol + *n*-alkane systems [32,53]. Consequently, only the (d, h) contacts remain to be determined (Table I).

3.1.5. DMSO + 1-Alkyne

These systems possess the (a, d), (a, y) and (d, y) contacts. The (a, y) contacts are represented by DIS and QUAC interchange coefficients calculated using experimental data for 1-alkyne + *n*-alkane systems [33]. So, only the (d, y) contacts must be fitted. Final values of the parameters are given in Table I.

3.2. Estimation of the Adjustable ERAS Parameters

The reduction parameters, V^* and P^* of the pure compounds are listed in Table II. The K_A, Δh^*_A, Δv^*_A parameters of 1-alkanols are determined from H^E and V^E data of their systems with *n*-alkane. The values used in this work are collected in Table II.

The remaining parameters K_{AB}, Δh^*_{AB}, Δv^*_{AB}, X_{AB} are adjusted to H^E and V^E data of 1-alkanols + DMSO mixtures. More details are given in literature [40,41]. Final parameters are listed in Table III.

TABLE II ERAS parameters of pure compounds at 298.15 K

Compound	K_i	P^*_i (J cm^{-3})	V_i (cm^3 mol^{-1})	V^*_i (cm^3 mol^{-1})	Δh^*_i (KJ mol^{-1})	Δv^*_i (cm^3 mol^{-1})
Methanol	986^a	443.6^d	40.73^g	32.13^d	– 25.1^a	– 5.6^a
Ethanol	317^a	426.4^d	58.67^g	47.11^d	– 25.1^a	– 5.6^a
1-propanol	197^a	433.9^d	75.16^g	61.22^d	– 25.1^a	– 5.6^a
1-butanol	175^b	422.7^d	91.97^d	75.70^d	– 25.1^a	– 5.6^a
1-pentanol	153^c	411.0^c	108.69^c	89.76^c	– 25.1^a	– 5.6^a
1-hexanol	120^b	431.1^e	125.19^e	103.52^e	– 25.1^a	– 5.6^a
DMSO	0	808.6^f	71.28^f	57.82^f	0	0

[a][40,41]; [b][21]; [c][41]; [d][40]; [e][64]; [f]calculated using α and κ_T from [27]; [g][65].

TABLE III ERAS parameters at 298.15 K for 1-alkanol + DMSO mixtures (this work)

1-Alkanol	Δh^*_{AB} (kJ mol^{-1})	Δv^*_{AB} (cm^3 mol^{-1})	K_{AB}	X_{AB} (J cm^{-3})
Methanol	−48.0	−17.0	4.2	2.0
Ethanol	−35.0	−17.0	1.5	32.0
1-Propanol	−33.0	−17.0	1.5	47.0
1-Butanol	−31.0	−21.0	1.5	51.0
1-Pentanol	−31.0	−21.0	1.2	51.0
1-Hexanol	−31.0	−21.0	1.0	51.0

TABLE IV Molar excess enthalpies, H^E, at equimolar composition and temperature *T*, of DMSO + organic solvent mixtures

Solvent	*T*(*K*)	*N*[a]	H^E (J mol^{-1})			dev(H^E)[b]				*Ref.*
			exp.	*DQ*[c]	*UNIF*[d]	*exp.*	*DQ*[c]	*UNIF*[d]	*ERAS*[e]	
C_6H_6	298.15	10	585	598	623	0.009	0.020	0.044		[18]
		13	589			0.029	0.032	0.051		[66]
		16	602			0.015	0.048	0.056		[14]
		31	587			0.007	0.022	0.039		[8]
	308.15	6	588	598	693	0.005	0.022	0.160		[18]
C_7H_8	303.15	10	857	830	900	0.013	0.090	0.047		[67]
Methanol	293.15	10	−348	−432	−381	0.057	0.187	0.130		[68]
	298.15	20	−350	−390	−374	0.008	0.074	0.066	0.257	[20]
		19	−391			0.003	0.038	0.033	0.166	[69]
Ethanol	293.15	9	410	363	263	0.078	0.244	0.290		[68]
	298.15	20	411	396	201	0.002	0.078	0.370	0.231	[20]
1-Propanol	293.15	8	707	657	755	0.044	0.184	0.150		[68]
	298.15	20	677	679	702	0.003	0.052	0.025	0.150	[20]
1-Butanol	298.15	18	857	860	1144	0.002	0.028	0.190	0.126	[20]
1-Pentanol	298.15	18	937	968	1555	0.008	0.041	0.360	0.093	[20]
1-Hexanol	298.15	18	1014	1023	1723	0.014	0.048	0.490	0.098	[20]
1-Hexyne	298.15	10	77	85		0.039	0.110		0.120[f]	[27]
1-Heptyne	298.15	10	248	285		0.065	0.130		0.140[f]	[27]
1-Octyne	298.15	10	390	417		0.020	0.062		0.067[f]	[27]
1-Nonyne	298.15	5	597	694		0.044	0.130			[70]

[a] number of experimental data points; [b] dev(H^E) = $\{1/N\sum[(H^E_{\text{exp}} - H^E_{\text{calc}})/|H^E_{\text{exp}}(x_1 = 0.5)|]^2\}^{1/2}$: N, number of data points; [c] DISQUAC calculations (this work); [d] UNIFAC results using parameters from [28,29]; [e] ERAS results (this work); [f] ERAS results with parameters from [27].

4. RESULTS AND DISCUSSION

4.1. Experimental Results

The large miscibility gaps (see below), with very high upper critical solution temperatures (UCST), of DMSO + alkane systems reveal that these solutions are characterized by strong dipole–dipole interactions between DMSO molecules. Note that DMSO has not only a large μ (4.06 D) [1], but also a large effective dipole moment ($\bar{\mu} = 1.84$), a very useful quantity to examine the impact of polarity on bulk properties [54,55]. This may explain that the H^E values of mixtures containing DMSO are normally quite large and positive (Table IV). Interactions between unlike molecules are only predominant in the DMSO + methanol system. In the DMSO + 1-hexyne mixture, molecular interactions between the two components might be comparable to the mean of those among the same molecules in the pure liquids before mixing.

NMP has a similar μ (4.09 D) [1] to that of DMSO. However, its $\bar{\mu}$, is lower (1.59), and the UCST (NMP + C_6H_{12}) = 283.10 K [56]. In contrast, the UCST (DMSO + C_6H_{12}) must be much higher (DISQUAC predicts 478 K) as the transition temperature at $x_1 = 0.011$ is 323 K [57]. This explain that for a given organic solvent, at equimolar composition and 298.15 K, H^E (DMSO) > H^E (NMP). Similarly, $\bar{\mu}$ (DMSO) > $\bar{\mu}$ (dimethylformamide, DMF) = 1.60 and H^E (DMSO) > H^E (DMF) except for systems including 1-alkanols [20]. This means that DMSO has a higher proton accepting ability than DMF when mixed with 1-alkanols [20].

It is interesting to remark that in 1-alkanol + DMSO, + DMF, or + NMP, the position of the H^E values are shifted to higher mole fractions of the second compound when the length of the 1-alkanol increases [4,20]. The opposite behaviour is encountered for mixtures formed by 1-alkanol and a non-polar compound (benzene), or a polar non-protonic solvent (cyclohexanone, 1,4-dioxane) [20].

4.2. Comparison of DISQUAC with Experimental Results

DISQUAC represents fairly well the rather complex behaviour of the studied mixtures as it is concluded from the comparison between experimental results for H^E, vapor–liquid equilibria (VLE), G^E, $\ln \gamma_i^\infty$ and $H_i^{E,\infty}$ with DISQUAC calculations shown along Tables IV–VII (see also Figs. 1–4). Particularly, it is noteworthy that the model describes quite accurately the C_p^E of the DMSO + benzene system (Fig. 4).

4.3. Comparison between DISQUAC and UNIFAC Results

Both models yield similar results on VLE (Table V). The mean relative standard deviation in pressure using UNIFAC and DISQUAC is about 3.6%. Usually, UNIFAC, due to the suitability of the semi-empirical combinatorial term applied [58], provides

TABLE V Molar excess Gibbs energies, G^E, at equimolar composition and temperature T, of DMSO + organic solvent mixtures

Solvent	*T(K)*	N^a	G^E (J mol^{-1})			$\sigma_r(P)^b$			*Ref.*
			exp	*DQ*^{c}	*UNIF*^{d}	exp	*DQ*^{c}	*UNIF*^{d}	
C_6H_6	298.15	11	825	832	818	0.007	0.017	0.023	[71]
		15	818			0.016	0.058	0.023	[72]
	313.15	11	809	844	825	0.005	0.028	0.018	[71]
		15	822		955	0.014	0.069	0.016	[72]
	353.15	6	904	875	913	0.002	0.021	0.056	[73]
C_7H_8	323.15	9	1050	1027	−720	0.007	0.094	0.079	[67]
Methanol	293.15	21	−723	−712	−743	0.007	0.014	0.018	[74]
	313.15	21	−740	−737	−515	0.008	0.019	0.020	[74]
Ethanol	333.15	24	−428	−495	−324	0.007	0.047	0.060	[75]
1-Butanol	423.45	21	−391	−264	−326	0.013^e	0.016^e	0.012^e	[76]
1-Pentanol	373.15	9	−183	−141		0.001	0.016	0.051	[77]
1-Hexyne	298.15	6	990	1004		0.006	0.014		[78]

^{a}Number of experimental data points; $^b\sigma_r(P) = \{1/N\sum[(P_{\exp} - P_{\text{calc}})/P_{\exp}]^2\}^{1/2}$; N, number of data points; ^{c}DISQUAC results (this work); ^{d}UNIFAC results using parameters from [28,29]; ^{e}Absolute mean deviation in mole fraction of the vapor-phase ($\Delta y = 1/N\sum|y_{\text{calc}} - y_{\exp}|$).

TABLE VI Natural logarithms of activity coefficients at infinite dilution in DMSO (1) + organic solvent (2) mixtures at temperature T

Solvent	T (K)	$\ln \gamma_1^\infty$			$\ln \gamma_1^\infty$			*Ref.*
		exp.	*DQ*[a]	*UNIF*[b]	*exp.*	*DQ*[a]	*UNIF*[b]	
n-C_6	283.15		4.15	4.93	5.41	4.65	4.66	[79]
	298.15		3.89	4.81	4.56	4.37	4.57	[79]
	303.15		3.80	4.76	4.21	4.28	4.24	[80]
	333.15		3.37	4.45	3.76	3.81	3.68	[80]
n-C_7	283.15		4.09	4.72	5.75	5.22	5.07	[79]
	298.15		3.83	4.60	5.01	4.90	4.71	[79]
	303.15		3.75	4.55	4.55	4.80	4.59	[80]
	333.15		3.32	4.24	4.06	4.26	3.95	[80]
n-C_8	283.15		4.03	4.56	6.18	5.77	5.48	[79]
	298.15		3.77	4.43	5.30	5.41	5.07	[79]
	303.15		3.69	4.38	4.97	5.30	4.94	[80]
	333.15		3.26	4.07	4.38	4.69	4.22	[80]
c-C_6	283.15		4.54		4.58	4.09		[79]
	298.15		4.26		3.83	3.85		[79]
c-C_7	283.15		4.49		4.84	4.28		[79]
	298.15		4.21		4.16	4.02		[79]
c-C_8	283.15		4.43		5.14	4.31		[79]
	298.15		4.16		4.34	4.05		[79]
C_6H_6	303.15		1.79	1.50	1.19	1.36	1.18	[80]
	333.15		1.68	1.40	1.10	1.27	1.01	[80]
Methanol	303.15		−1.28	−1.36	−0.95	−0.98	−0.93	[80]
	333.15		−1.29	−1.35	−0.83	−0.95	−0.88	[80]
Ethanol	303.15		−0.60	−1.21	−0.38	−0.57	−0.53	[80]
	333.15		−0.70	−1.21	−0.49	−0.64	−0.51	[80]
1-Propanol	303.15		−0.30	−0.87	−0.21	−0.25	−0.34	[80]
	333.15		−0.41	−0.95	−0.36	−0.36	−0.39	[80]
1-Hexyne	283.15		2.38		2.30	1.58		[79]
	298.15		2.40		1.79	1.57		[79]
1-Heptyne	283.15		2.51		2.70	2.06		[79]
	298.15		2.50		2.23	2.03		[79]
	303.15	1.90	2.49			2.02		[81]
	313.35	1.71	2.47			1.99		[81]
1-Octyne	283.15		2.59		3.19	2.53		[79]
	298.15		2.57		2.54	2.49		[79]
	313.37	2.10	2.52			2.44		[81]
	322.90	2.01	2.49			2.40		[81]

[a]DISQUAC calculations (this work); [b]UNIFAC results using parameters from [28,29].

better results on $\ln \gamma_i^\infty$ than DISQUAC. Nevertheless, for the present mixtures, the two models yields similar results on $\ln \gamma_i^\infty$ (mean deviation ≈ 18%).

In contrast, DISQUAC substantially improves UNIFAC results on H^E (Table IV; Fig. 2). The mean deviations are 7.5 and 15.5%, respectively. Consequently, results on $H_2^{E,\infty}$ of DMSO (1) + organic solvent (2) mixtures (Table VII) are also improved by DISQUAC. Finally, it should be noted that the temperature dependence of the thermodynamic properties is also better described by DISQUAC (see Fig. 4).

4.4. Comparison between DISQUAC and ERAS Results

Table IV compares H^E values from both models for 1-alkanol + DMSO mixtures. ERAS results are particularly poor for the solutions containing the shorter 1-alkanols. This is mainly due to the symmetry of the H^E curves which is not well reproduced as the

TABLE VII Partial excess molar enthalpies at infinite dilution and at 298.15 K of DMSO (1) + organic solvent (2) mixtures

Solvent	$H_1^{E,\infty}$ (kJ mol^{-1})			$H_2^{E,\infty}$ (kJ mol^{-1})			*Ref.*
	exp.	*DQ*[a]	*UNIF*[b]	*exp.*	*DQ*[a]	*UNIF*[b]	
n-C_6		12.17	6.72	13.31	13.20	15.19	[82]
n-C_7		12.17	6.72	15.15	15.04	17.36	[82]
C_6H_{12}		13.00		11.38	11.32		[82]
C_6H_6		2.77	2.52	2.64	2.57	2.31	[82]
C_7H_8		3.04	3.51	3.77	4.00	3.15	[82]
methanol		− 0.36	− 0.40	− 1.42	− 1.25	− 1.58	[82,83]
				− 1.38			[84]
ethanol		2.26	1.64	1.17	1.68	0.54	[83]
				1.21			[83]
1-propanol		2.64	3.18	2.55	2.72	2.43	[82,83]
1-butanol		3.06	3.89	3.97	3.84	4.39	[82]
				4.14			[83]
1-pentanol		3.44	4.20	5.40	4.48	6.39	[83]
				5.56			[84]

[a]DISQUAC calculations (this work); [b]UNIFAC results using parameters from [28,29].

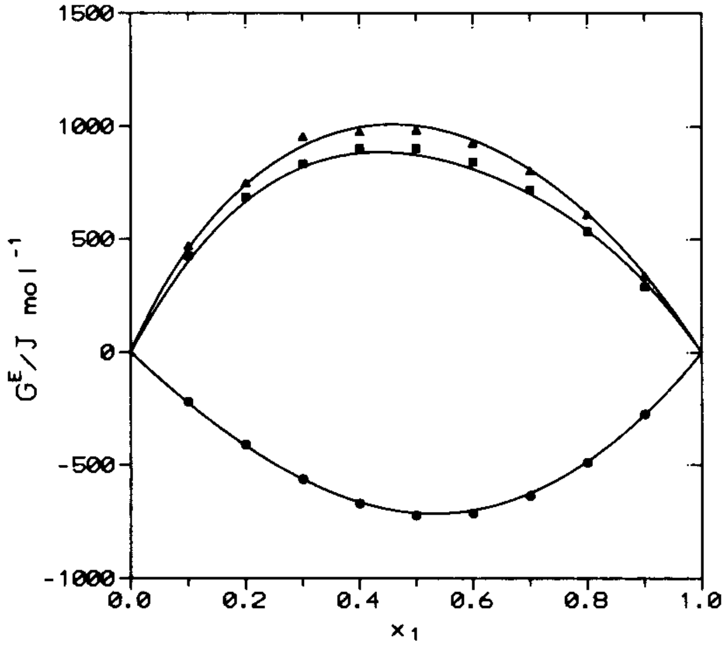

FIGURE 1 G^E for some mixtures containing DMSO. Lines, DISQUAC calculations. Symbols, experimental results: (●), methanol (1) + DMSO (2) at 313.15 K [74]; (■) DMSO (1) + benzene (2) at 353.15 K [73]; (▲), DMSO(1) + 1-hexyne at 298.15 K [78].

contribution to H^E from the self-association of the 1-alkanol is too shifted to higher concentrations in DMSO. So, from the point of view of ERAS, there is a overestimation of the self-association of the alkanol molecules, while the physical interactions are really more important. In contrast, this situation is better represented by the model

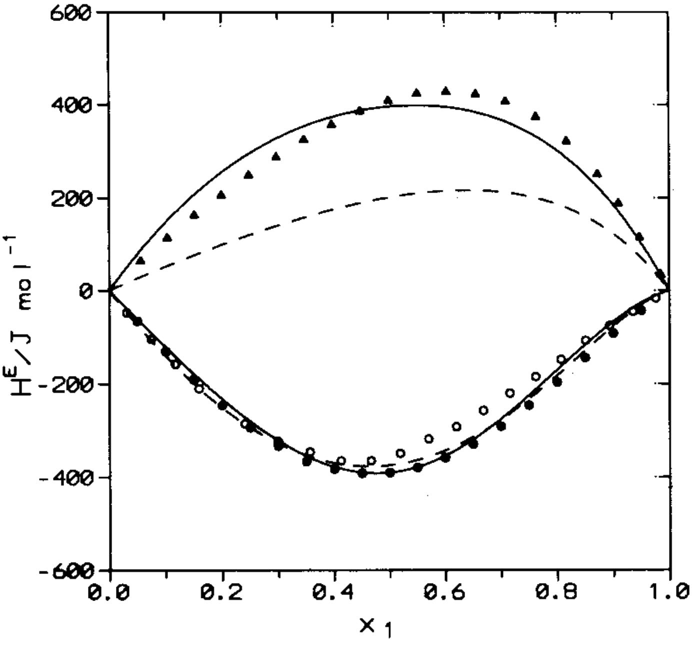

FIGURE 2 H^E for 1-alkanol (1) + DMSO (2) mixtures at 298.15 K. Solid lines, DISQUAC calculations; dashed lines, ERAS results. Symbols, experimental values: methanol, (●) [69]; (O) [20]; (▲), ethanol [20].

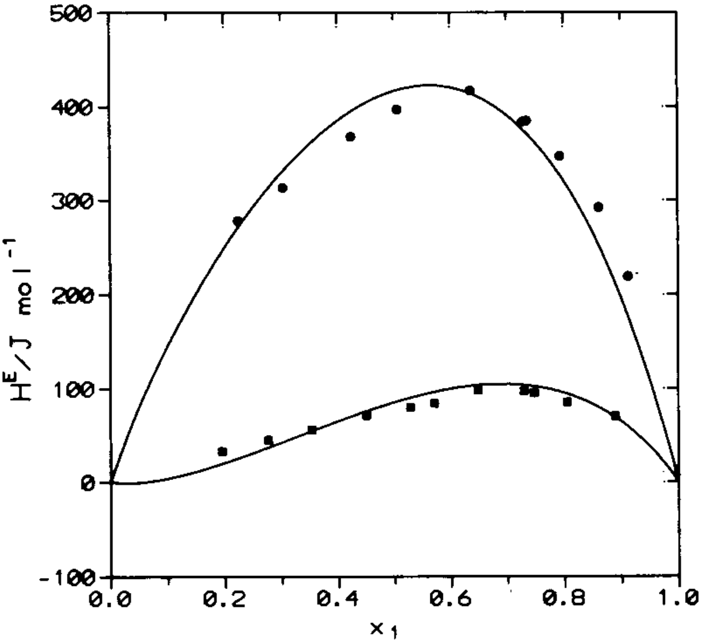

FIGURE 3 H^E for DMSO (1) + 1-alkyne (2) mixtures at 298.15 K. Solid lines, DISQUAC calculations. Symbols, experimental values [27]: (■), 1-hexyne (●), 1-octyne.

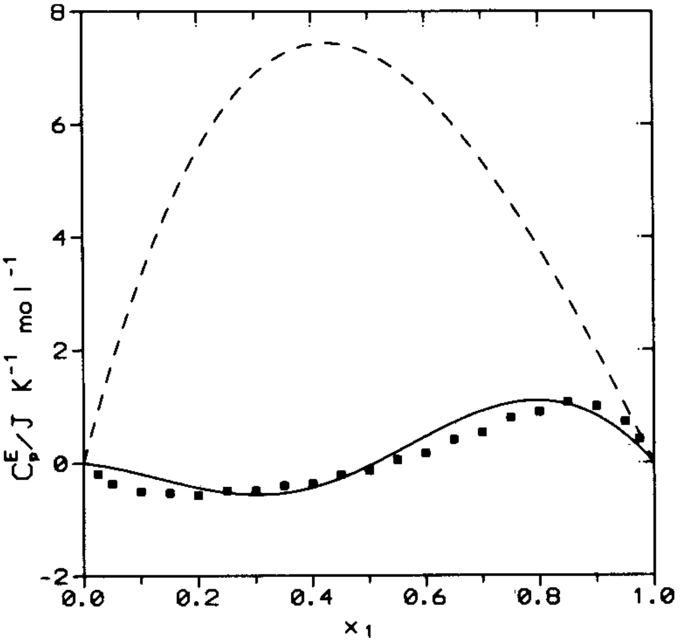

FIGURE 4 C_p^E for the benzene (1) + DMSO (2) mixture at 298.15 K. Solid line, DISQUAC calculation, dashed line, UNIFAC result. Symbols, experimental values [12].

for systems with longer 1-alkanols, characterized by low K_A and large X_{AB} values. Nevertheless, the model provides a quite satisfactory description of the V^E curves (Fig. 5). So, for the methanol, or 1-hexanol + DMSO systems, ERAS predicts $V^E(x_l = 0.5, 298.15\,\mathrm{K}) = -\ 0.536$ and $0.333\,\mathrm{cm^3\,mol^{-1}}$, respectively. The experimental values are (in the same order as above) -0.58 [59] and $0.326\,\mathrm{cm^3\,mol^{-1}}$ (value at 303.15 K [60]).

DMSO + 1-alkyne solutions have been treated in the framework of ERAS assuming that the two compounds are self-associated and that cross association between them exists [27]. Table IV shows a comparison between ERAS results obtained in this way and DISQUAC calculations. Both models yield similar results. In comparison with 1-alkanol + DMSO mixtures, there is an improvement of the H^E results, which may be ascribed to the calculations developed considering a very low self-association of the mixture components. For example, for 1-hexyne, $K_A = 0.20$; $\Delta h_A^* = -12.0\,\mathrm{KJ\,mol^{-1}}$ and $\Delta v_A^* = -3.0\,\mathrm{cm^{-3}\,mol^{-1}}$ [27], and for DMSO, $K_A = 0.35$; $\Delta h_A^* = -25.0\,\mathrm{KJ\,mol^{-1}}$ and $\Delta v_A^* = -4.80\,\mathrm{cm^{-3}\,mol^{-1}}$ [27].

4.5. The Interaction Parameters

In DMSO + 1-alkanol systems, the $C_{\mathrm{dh},l}^{\mathrm{QUAC}}$ ($l = 1,3$) coefficients are independent of the alkanol. The enthalpic QUAC parameters are only different for the lower alcohols (Table I). Similar trends have been observed in other alcoholic solutions, e.g, 1-alkanol + *n*-alkane [32,53], + benzene [52], + CCl_4 [61], + triethylamine [50], + NMP [4]. This reveals the different character (stronger self-association, higher

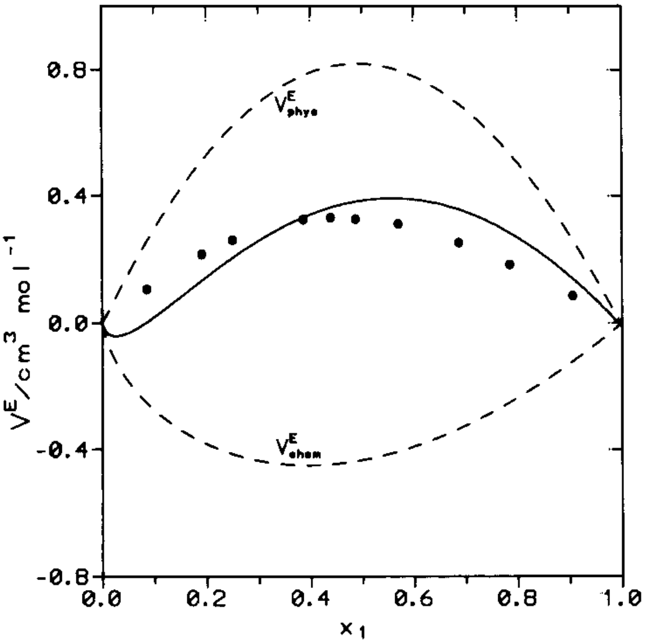

FIGURE 5 V^E for 1-hexanol (1) + DMSO (2) mixture at 303.15. Solid line, ERAS result; dashed lines physical and chemical contributions to V^E. Symbols, experimental values [60].

dielectric constant) of first members of homologous series when compared to the longer ones. Similar effects appear when treating 1-alkanol + benzene [62] or + CCl_4 [63] in terms of Barker's theory.

Moreover, the $C^{QUAC}_{dy,l}$ ($l = 1,2,3$) coefficients are independent of the 1-alkyne. The same occurs in sulfolane [3] or NMP [4] + 1-alkyne, or in sulfolane + nitrile where the QUAC parameters are independent of the nitrile [3]. This seems to be a quite general trend in the DISQUAC model, which makes the determination on the interaction parameters easier.

5. CONCLUSIONS

DISQUAC interaction parameters are given for the following contacts: SO/alkane, SO/aromatic; SO/hydroxyl and SO/alkyne. DISQUAC represents fairly well as a complete set of thermodynamic properties (H^E, G^E, VLE, $\ln \gamma_i^\infty$ and $H_i^{E,\infty}$). DISQUAC improves UNIFAC calculations for H^E. Both models yield similar results for VLE. In addition, DISQUAC also improves ERAS results for 1-alkanol + DMSO mixtures. This may be due to ERAS cannot represent the strong dipole–dipole interactions present in such solutions.

The $C^{QUAC}_{dh,l}$ ($l = 1,3$) coefficients are independent of the 1-alkanol. The QUAC enthalpic parameters is only different for methanol or ethanol. Similarly in DMSO + 1-alkyne, $C^{QUAC}_{dy,l}$ ($l = 1,2,3$) coefficients are independent of the alkyne.

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