Mixing Enthalpies of Six Binary Systems Involving Sulfolane over the Entire Composition Range, at 303.16 K

Michele Pansini and Liliana Jannelli*

Thermodynamics Section, The Institute of Chemistry—Faculty of Engineering, The University of Naples, Naples, Italy

Enthalpimetric behavior of six binary systems involving sulfolane was accurately investigated over the entire composition range, at 303.16 K, the other component being a polar substance (dimethyl sulfoxide, nitrobenzene, benzonitrile) or a nonpolar substance (carbon tetrachloride, dioxane, benzene). The H^E-composition curves markedly differ from each other, the different sizes, shapes, and properties of molecules reflecting their effects on interactions of any kind. However, the magnitude of the H^E values allows us to conclude that these interactions are of moderate importance and hence the selected systems may be classified as regular and not quite athermal mixtures. A reliable interpretation of H^E data rests in the superimposition and alternative predominance of at least three factors: ordinary exchange energies and destructuration of the self-associate component, both resulting in positive H^E values, and electrostatic interactions (dipole–dipole and dipole–induced dipole interactions) which result in negative H^E values.

Introduction

Previous data on excess properties of some binary systems involving sulfolane + benzene (*1, 2*), + carbon tetrachloride (*1, 3*), + dioxane (*1, 4*), + dimethyl sulfoxide (*5*), + nitrobenzene (*6, 7*), and + benzonitrile (*8*) allowed us to classify them among regular mixtures in the sense of Hildebrand; volumes and dielectric constants on mixing exhibit indeed scarcely noticeable deviations from ideal values, which may be calculated on the basis of a linear dependence of solutions properties on composition (mole or volume fraction); furthermore, an accurate thermal analysis on solid–liquid phase equilibria of these binary systems was carried out over the entire composition range, and rational activity coefficients of components were drawn which do not noticeably differ from unity and this in spite of a large scattering of properties of selected substances. (The deviations are slightly more noticeable in the case of the benzene (1)–sulfolane (2) system.)

In the case of dioxane–sulfolane and carbon tetrachloride–sulfolane systems some solid AB_2 or AB compounds were observed (*3, 4*); in the latter case the compound is not soluble.

Molar volumes of selected substances do not markedly differ from each other (86–103 cm³·mol⁻¹ at 25 °C), the exception being dimethyl sulfoxide ($V = 71.3$ cm³·mol⁻¹). Carbon tetrachloride is a globular molecule with an approximately central force field and with acceptor properties arising from incomplete 3d orbitals. Dioxane is a protic solvent in which most of the molecules are in the so-called chair form and the cancellation of the COC moments results in a zero moment; dimethyl sulfoxide is a distorted tetrahedral molecule with a fairly high dipole moment (3.96 D) of which the negative end is exposed. Benzene, nitrobenzene, and benzonitrile molecules are flattened by resonance; nitrobenzene and benzonitrile molecules however are characterized by a fairly high dipole moment ($\mu = 4.0$ D),

whereas benzene is a symmetric molecule with a moderate polarizability. Sulfolane, as already pointed out, is a globular molecule with a large dipole moment (4.8 D) of which only the negative end is exposed.

The inert role of sulfolane as solvent and the above-cited regular behavior of its solutions was ascribed to the low accessibility of its dipole because of the steric hindrance of the globular molecule, which prevents remarkable interactions of any kind.

In order to complete the picture of the thermodynamic behavior of the above catalogued binary systems and to evidence and differentiate the influence of the volume, shape, and polarity of molecules on exchange energies of components in mixtures, we report here data on mixing enthalpies of sulfolane with each of the above selected substances, at 303.16 K, over the entire composition range.

Experimental Section

Materials. Sulfolane, kindly supplied by Shell Italia, was accurately purified, dried, and degassed as usually reported (*1, 8*).

Carbon tetrachloride was distilled over calcium chloride, dried over P_2O_5, and then fractionally distilled.

Benzene was partially frozen, about half was discarded as unfrozen liquid, and then fractionally distilled over anhydrous sodium sulfate.

Dioxane was fractionally crystallized, dried carefully over sodium pellets, and then fractionally distilled.

Nitrobenzene and *benzonitrile* were purified by repeated distillation under vacuum over phosphorus pentoxide. Only freshly distilled product was used in preparing solutions.

Dimethyl sulfoxide was distilled repeatedly under reduced pressure. Then the collected product was stored over molecular sieves (5 Å type) at least 48 h and distilled under vacuum shortly before use.

The purity of the substances tested by gas–liquid chromatographic analysis was better than 99.8%.

Properties of purified samples (Table I) strictly agree with the most reliable literature data (*9–11*) and with our previous data (*1–8*).

Apparatus. Excess mixing enthalpies of selected binary mixtures were determined in a LKB flow calorimeter (Model 2107-212) using the auxiliary equipment and operating procedure described by Benson and Grolier (*12*).

Studies of test systems guaranteed a precision better than 1% over most of the mole fraction range. A calibration was carried out before and after each run. All measurements were carried out at 303.16 ± 0.005 K because at temperature below 301.16 K sulfolane is solid.

For the sake of uniformity with previous works, sulfolane is indicated as component 2.

Results

Table II and Figure 1 record values of excess mixing enthalpies, H^E (J·mol⁻¹), measured at 303.16 K, over the entire composition range, for the six selected systems. In the case of benzene (1)–sulfolane (2) system the experimental values by

*Corresponding address: Istituto di Chimica, Facoltà di Ingegneria dell'-Università, Napoli—Piazzale Tecchio, Italy.

Table I. Description and Physical Properties of Component Liquids

component	source	d (298.16 K)/g·cm⁻³		mp/K	
		obsd	lit.	obsd	lit.
carbon tetrachloride	Carlo Erba RSE	1.584 35	1.584 39 (9)		
nitrobenzene	J. T. Baker Chemical B.V., Analyzed reagent	1.198 17	1.98 35 (9)		
dioxane	BDH Chemical Ltd., analytical reagent	1.027 86	1.027 97 (9)		
dimethyl sulfoxide	Rudi Pont Reagent Grade	1.095 65	1.095 58 (9)		
benzene	Carlo Erba RPE	0.873 66	0.873 70 (9)		
benzonitrile	Fluka A.G. Puriss	1.000 58	1.00 06 (9)		
sulfolane	Shell Italia	1.262 30ᵃ	1.262 30 (11)	301.61	301.61 (9), 301.78 (11)

ᵃSulfolane data refer to 303.16 K.

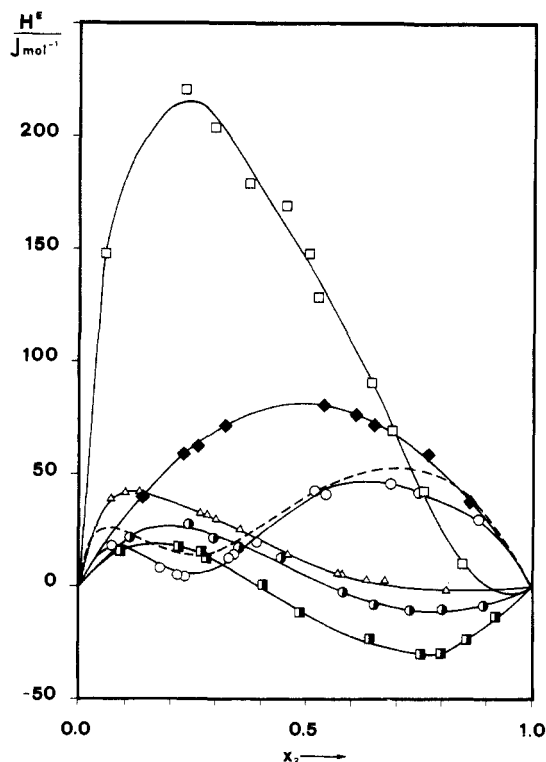**Figure 1.** H^E-composition plots (x_2 = sulfolane mole fraction) for carbon tetrachloride (1)–sulfolane (2), □; dimethyl sulfoxide (1)–sulfolane (2), ◆; benzene (1)–sulfolane (2), O; dioxane (1)–sulfolane (2), △; nitrobenzene (1)–sulfolane (2), ◑; benzonitrile (1)–sulfolane (2), ◨; dashed line refers to Karvo's data.

Karvo (13) at 303.16 K are also plotted in the diagram (dashed line); both sets of data are in good qualitative agreement. An interesting feature of both these H^E-composition curves is a relatively broad minimum at $0.2x_2$ with a maximum on the other side, a scarcely noticeable one in a region close to pure benzene, not exceeding 18 J·mol⁻¹ and a more remarkable maximum (45 J·mol⁻¹) at $0.65x_2$.

The dioxane (1)–sulfolane (2) system exhibits very low negative H^E values in a small region close to pure sulfolane, and mixing enthalpies become positive and more remarkable with decreasing sulfolane content in solution and exhibit a maximum, not exceeding 45 J·mol⁻¹, in the region richer in dioxane ($x_2 = 0.1$).

The carbon tetrachloride (1)–sulfolane (2) system shows more remarkable positive enthalpies than any of the selected systems; these steadily decrease until zero, at $x_2 = 0.8$, with increasing sulfolane content, starting from a sharp maximum (220 J·mol⁻¹) occurring in the carbon tetrachloride-rich region (0.23x_2).

The dimethyl sulfoxide (1)–sulfolane (2) system is characterized by a quadratic curve with a sharp maximum (80 J·mol⁻¹) occurring approximately at $x_2 = 0.5$.

The nitrobenzene (1)–sulfolane (2) system exhibits an S-shaped curve, with low positive H^E values (~26 J·mol⁻¹) in the

Table II. Experimental Molar Excess Enthalpies, H^E, at 303.16 K

x_2	H^E/J·mol⁻¹	x_2	H^E/J·mol⁻¹
x_2Sulfolane + (1 − x_2)Carbon Tetrachloride		0.6370	3.8₀
		0.6753	2.9₉
		0.8243	−1.7₇
0.1049	148.3₁		
0.1809	204.3₀	x_2Sulfolane + (1 − x_2)Dimethyl Sulfoxide	
0.2289	221.8₄		
0.2901	204.1₇	0.1429	41.6₇
0.3769	179.1₂	0.2326	57.9₃
0.4576	169.2₀	0.2644	62.3₀
0.5048	148.8₂	0.3231	71.0₀
0.5258	128.6₆	0.5424	81.9₆
0.6450	91.8₁	0.6100	75.8₈
0.6913	69.0₉	0.6527	71.0₀
0.7556	42.9₁	0.7730	60.2₅
0.7580	40.0₀	0.8575	36.7₇
0.8446	10.2₃		
		x_2Sulfolane + (1 − x_2)Benzene	
x_2Sulfolane + (1 − x_2)Nitrobenzene		0.0685	18.5₉
0.1172	21.9₃	0.1757	7.2₂
0.2102	25.7₄	0.2156	5.4₆
0.2426	27.5₃	0.2223	10.8₅
0.2960	20.7₄	0.3282	13.9₀
0.3533	17.7₅	0.3383	15.7₁
0.4477	13.3₄	0.3929	17.1₅
0.5841	−2.0₅	0.5205	45.8₇
0.6470	−8.9₀	0.5429	40.3₄
0.7290	−9.6₂	0.6877	45.7₇
0.7812	−11.0₂	0.7453	43.0₀
0.8025	−10.4₄	0.8804	30.2₀
0.8941	−9.0₁		
		x_2Sulfolane + (1 − x_2)Benzonitrile	
x_2Sulfolane + (1 − x_2)Dioxane		0.0862	15.8₆
0.0728	38.5₁	0.2240	16.9₉
0.0994	43.3₈	0.2682	15.2₆
0.1334	40.6₄	0.2768	12.7₉
0.2650	32.1₃	0.4066	−0.3₃
0.2825	32.7₁	0.4880	−11.9₇
0.2973	29.6₄	0.6434	−23.1₆
0.3541	24.1₉	0.7550	−30.2₂
0.4622	14.9₅	0.8000	−29.8₂
0.4637	14.1₇	0.8560	−23.8₀
0.5718	5.2₂	0.9234	−14.6₈
0.5764	5.3₈		

nitrobenzene-rich region and even less remarkable negative values in the sulfolane-rich region. The same behavior may be observed for the benzonitrile (1)–sulfolane (2) system but exothermic effects are more remarkable.

The experimental data for the six systems were fitted by a least-squares computer program to a smoothing function:

$$H^E = x_1x_2 \{A + B(x_2 - x_1) + C(x_2 - x_1)^2 + D(x_2 - x_1)^3 + E(x_2 - x_1)^4 + \cdots\} \quad (1)$$

Each point was assigned unit weight.

The parameters of the smoothing equations, their standard deviations σ, and the standard deviations $\sigma(H^E)$ of the molar

excess enthalpies are given in Table III.

Discussion

The magnitude of H^E values allows all the selected systems to be classified as regular and not quite athermal mixtures.

Let us suppose that all interactions among components may reduce to ordinary exchange energies; hence positive H^E values and quadratic H^E–composition curves should be expected. This is the case of dimethyl sulfoxide (1)–sulfolane (2) system; that only the negative end of dipoles of both these molecules is exposed indeed prevents interactions of any kind including dipolar interactions.

In the case of nonpolar–polar systems, with increasing sulfolane content in solution, the presence of strong dipoles in a considerable amount results in an increase of the number of polarized molecules of the other component. Hence the effects on H^E of interactions of the dipole of sulfolane with the polarizable chlorine atoms of carbon tetrachloride or the oxygen atoms of dioxane may not be neglected any more. The superimposition and the steady predominance of these effects (negative H^E) on effects of ordinary exchange energies (positive H^E) results in a steady decrease of H^E values with increasing sulfolane content in solution. Hence the maximum in H^E–X_2 curves is shifted toward the apolar component richer region, whereas negative values of H^E may be predicted and even taken in a region close to pure sulfolane, where polarization effects are more noticeable; the very sharp maximum (220 $J \cdot mol^{-1}$) at $0.3x_2$ in the case of the sulfolane–carbon tetrachloride system may be indicative of a steeply increasing repulsion of molecules, with decreasing sulfolane content, which results in a likely phase separation, as is the case (*3*) at 284.16 K.

As recommended by Rowlinson (*14*) the formation of solid molecular compounds (sulfolane (2)–dioxane (1) and carbon tetrachloride (1)–sulfolane (1)) cannot be indicated as a reliable criterion for supposing unusually intensive interactions between components. The solid compound formation can rather be ascribed to an accidental favorable crystalline geometry. Evidences for this supposition are supplied by the miscibility of components in the solid phase, the insolubility of the carbon tetrachloride–sulfolane compound in liquid solutions, and by the low melting temperature of compound with respect to the melting points of components (only carbon tetrachloride with mp = 250 K melts at a lower temperature than the molecular compound).

In the case of the benzene–sulfolane system the presence of the minimum at $x_2 = 0.2$ should be indicative that corresponding to this composition a concurrence of favorable events results in a casual predominance of the effects of dipole–induced dipole interactions on exchange energies of any kind. Presumably the benzene ring may be polarized easier than carbon tetrachloride and dioxane molecules, even if the induced dipole should be less strong. Then with increasing sulfolane content in solution the effect of the increased number of polarized benzene molecules is counterbalanced in excess by the weakening and breaking of dipole–induced dipole interactions because of the increased dielectric constant of the medium; hence the sharp maximum in the H^E–composition curve in the region richer in sulfolane.

This interpretation is substantiated by the conclusions of Karvo (*13*, *15*) who exhaustively and extensively investigated aromatic hydrocarbon–sulfolane systems. (The measured positive H^E values reported by Karvo, which otherwise increase with temperature and the number of CH_3 groups in the molecule, were interpreted in terms of weak dipolar interactions, disturbed by steric hindrance of CH_3 groups and temperature.)

Finally the S-shaped H^E–composition curves in the case of strongly polar components (1) as nitrobenzene and benzonitrile

Table III. Parameters, the Standard Deviations, σ, of the Smoothing Equations (Eq 1), and Standard Deviations, $\sigma(H^E)$, for the Molar Excess Enthalpies at 303.16 K

system	$A \pm \sigma$	$B \pm \sigma$	$C \pm \sigma$	$D \pm \sigma$	$E \pm \sigma$	$F \pm \sigma$	$\sigma(H^E)/$ $J \cdot mol^{-1}$
sulfolane							
+ carbon tetrachloride	581.670 ± 15.676	−616.209 ± 94.662	470.350 ± 161.773	−165.947 ± 586.446	−138.950 ± 322.306	1772.04 ± 824.170	6.7$_6$
+ nitrobenzene	21.480 ± 3.968	−194.495 ± 4.712	67.828 ± 12.399				1.7$_0$
+ dioxane	43.321 ± 4.697	−183.245 ± 18.737	226.546 ± 73.977	312.644 ± 144.475	−47.637 ± 161.867	−948.776 ± 249.174	1.0$_4$
+ dimethyl sulfoxide	323.755 ± 4.368	−10.737 ± 9.066					2.1$_4$
+ benzene	156.904 ± 9.761	264.656 ± 26.366	−278.598 ± 78.759	−303.161 ± 56.129	669.658 ± 115.840		3.7$_8$
+ benzonitrile	−45.635 ± 5.136	−238.532 ± 10.371	7.388 ± 34.766	−12.923 ± 19.741	80.737 ± 45.519		1.6$_1$

are indicative that interactions between like and unlike molecules are competitive in strength. Then sulfolane, at low concentrations, limits its role to a disturbing effect on self-association of the component (1) (positive H^E values); but with increasing sulfolane content, strond dipolar interactions between the two substances result in negative H^E values. Interactions should be more intensive in the case of benzonitrile than nitrobenzene according to a more favorable geometry of the molecule.

Registry No. Sulfolane, 126-33-0; dimethyl sulfoxide, 67-68-5; nitrobenzene, 98-95-3; bezonitrile, 100-47-0; carbon tetrachloride, 56-23-5; dioxane, 123-91-1; benzene, 71-43-2.

Literature Cited

(1) Sacco, A.; Jannelli, L. *J. Chem. Thermodyn.* **1972**, *4*, 191.
(2) Jannelli, L.; Sacco, A. *J. Chem. Thermodyn.* **1972**, *4*, 715.
(3) Sacco, A.; Inglese, A.; Ciani, P.; Dell'Atti, A.; Rakshit, A. K. *Thermochim. Acta* **1976**, *15*, 71.
(4) Jannelli, L.; Inglese, A.; Sacco, A.; Ciani, P. *Z. Naturforsch. A* **1975**, *30A*, 87.
(5) Jannelli, L.; Pansini, M. *J. Chem. Eng. Data* **1965**, *30*, 428.
(6) Jannelli, L.; Azzi, A.; Lopez, A.; Saiello, S. *J. Chem. Eng. Data* **1960**, *25*, 77.
(7) Jannelli, L.; Lopez, A.; Jalenti, R.; Silvestri, L. *J. Chem. Eng. Data* **1982**, *27*, 28.
(8) Jannelli, L.; Lopez, A.; Saiello, S. *J. Chem. Eng. Data* **1980**, *25*, 259.
(9) Riddick, A. J.; Bunger, W. B. "Techniques of Chemistry", 3rd ed.; Weissenberg, A., Ed.; Wiley Interscience: New York, 1970; Vol. II.
(10) Covington, A. K.; Dickinson, T. "Physical Chemistry of Organic Solvent Systems"; Plenum Press: London, 1973; p 244.
(11) Martinmaa, J. J. *Suom. Kemistil. B* **1969**, *42*, 33.
(12) Kiyohara, O.; Benson, G. C.; Grolier, J. P. E. *J. Chem. Thermodyn.* **1977**, *9*, 315.
(13) Karvo, M. *J. Chem. Thermodyn.* **1980**, *12*, 635.
(14) Rowlinson, J. S. "Liquids and Liquid Mixtures"; Butterworth: London, 1959; p 158.
(15) Karvo, M. *J. Chem. Thermodyn.* **1983**, *15*, 821.

Infinite-Dilution Partition Coefficients for Haloalkane Solutes in Squalane–Dinonyl Phthalate Solvent Mixtures at 30.0 °C

Ghassan A. Oweimreen

Department of Chemistry, University of Petroleum and Minerals, Dhahran, 31261, Saudi Arabia

Using gas–liquid chromatography, we obtained infinite-dilution partition and activity coefficients at 30.0 °C for n-pentane and six haloalkane solutes in pure squalane, in pure dinonyl phthalate, and in five mixtures thereof. Where appropriate the results are contrasted with those from previous studies. Partition coefficients were found to differ by as much as 10% from those calculated from the partition coefficients for the pure single solvents by using the Purnell–Andrade equation. Theoretical expressions derived by Harbison et al. fitted the data within experimental error and were used to calculate interaction parameters. The results indicated the existence of a weak 1:1 complex between each of the haloalkane solutes and dinonyl phthalate. The association constants of these complexes were evaluated and their trends were qualitatively interpreted.

Introduction

For a variety of gas–liquid chromatographic (GLC) systems in which a volatile solute component (A) is distributed between a binary nonvolatile solvent mixture (B + C) and the gas phase, Purnell and de Andrade (1) find that the linear relation

$$K^0_{R(M)} = \phi_B K^0_{R(B)} + \phi_C K^0_{R(C)} \tag{1}$$

is obeyed within experimental error. $K^0_{R(B)}$ and $K^0_{R(C)}$ are the infinite-dilution solute partition coefficients in pure B and C, respectively. $K^0_{R(M)}$ is the infinite-dilution solute partition coefficient in a mixture where the volume fractions of B and C are ϕ_B and ϕ_C, respectively. On the other hand Harbison et al. (2) derive the expression

$$\ln K^0_{R(M)} = \phi_B \ln K^0_{R(B)} + \phi_C \ln K^0_{R(C)} + (\bar{V}_A/\bar{V}_B)\chi_{C(B)}\phi_B\phi_C \tag{2}$$

which, in general, predicts curvature in plots of $K^0_{R(M)}$ vs. ϕ_C.

$\bar{V}$ represents molar volumes, and $\chi_{C(B)}$ is the Flory-type interaction parameter characterizing B–C interactions.

While eq 1 (and extensions of it to solvents of up to five components (3)) has been used in the window diagram method (3–5) for optimizing chromatographic separations, several studies (2, 6–10) have shown that it remains an approximate description of the true physical situation. In these studies nonlinear $K^0_{R(M)}$ vs. ϕ_C plots were obtained. In two of these studies (2, 10) eq 2 fitted the results to within experimental error.

In this study infinite-dilution partition coefficients were obtained at 30.0 °C from GLC for n-pentane and six haloalkane solutes in squalane (SQ)–dinonyl phthalate (DNP) solvent mixtures. For all the solutes studied plots of $K^0_{R(M)}$ vs. ϕ_C were nonlinear. The results were analyzed and discussed in light of the treatment of Harbison et al. (2).

Experimental Section

Squalane (SQ) and di-n-nonyl phthalate (DNP) were used as received from Applied Science and Eastman, respectively. High-purity solutes were also used as received from standard suppliers. The stationary liquids and their mixtures were deposited on Chromosorb W (60/80 mesh, acid-washed and DMCS treated) solid support from solutions in methylene chloride. The methylene chloride was removed by rotary evaporation. Traces of methylene chloride were removed from the coated supports by placing them in a vacuum desiccator for several days. The free-flowing powders were then packed into previously coiled 1-m-long and 0.25-in.-o.d. stainless steel columns. The weight percent of the liquid phase employed was in the neighborhood of 10% and was determined from the weight loss of three separately ashed samples (ca. 1 g each) of coated support (11). Seven different columns were used at 30.0 °C with the following volume fractions of DNP (ϕ_C) in the solvent mixture: 0.000, 0.231, 0.410, 0.583, 0.671, 0.851, and 1.000. The solutes studied are listed in Table I.