Thermochimica Acta, 15 (1976) 71–78
© Elsevier Scientific Publishing Company, Amsterdam – Printed in Belgium

THERMODYNAMIC AND PHYSICAL PROPERTIES OF CARBON TETRACHLORIDE+SULFOLANE MIXTURES

A. SACCO, A. INGLESE, P. CIANI, A. DELL'ATTI AND A. K. RAKSHIT
Institute of Physical Chemistry, The University, Bari (Italy)

(Received 29 September 1975)

ABSTRACT

The solid+liquid phase diagram, drawn from thermal and dielectric measurements, is presented. It exibits a miscibility gap at $0.08 \leqslant x_2 \leqslant 0.58$, and two eutectics. The occurrence of a (likely 1:1) intermediate compound, which decomposes on melting into two immiscible liquids, is postulated. Mixed crystals are observed in the sulfolane richer region.

Deviations of the liquid mixtures from ideality, positive in the case of viscosity and negative in the case of dielectric constants, are evidenced.

1. INTRODUCTION

As a part of a research[1–7] on the physico-chemical properties of binary mixtures involving sulfolane (tetrahydrothiophene-1:1-dioxide) we present herewith the phase diagram, and transport and dielectric constant data of carbon tetrachloride(1)+sulfolane(2) mixtures over the entire composition range at 303.15, 313.15 and 323.15 K. Owing to the similarity of the molecular shapes and sizes of the components[4], this system may be selected to test the validity of current theories on solutions; sulfolane acts as an aprotic solvent with a fairly high dipole moment (4.8 D)* with only the negative end of the dipole exposed[2], whereas carbon tetrachloride is a so-called inert solvent with an approximately central force field.

2. EXPERIMENTAL

Chemical purification, and experimental details were described elsewhere[2,5]. As for dielectric constants measured on solid systems, care was taken to prevent inclusion of water vapor and cracks; while gas pockets were also avoided by evacuation.

---

*D = 3.336×10^{-30} Cm.

3. RESULTS

Phase diagram

Figure 1 shows the liquid + solid phase diagram as taken by thermal analysis with increasing and decreasing temperature (data in Table 1). The melting points of the pure components strictly agree with literature data[2,8]. The diagram is characterized by two eutectics at $x_2 = 0.01$ and $T = 250.2 \pm 0.1$ K, and $x_2 = 0.808$ and $T = 278.1 \pm 0.1$ K; the mixtures where $0.08 \leqslant x_2 \leqslant 0.58$ melt at constant temperature ($T = 284.6 \pm 0.2$ K). Such a diagram, of a kind which is otherwise seldom observed[9], points to a compound which melts incongruently into the immiscible liquids $L_1(x_2 = 0.08)$ and $L_2(x_2 = 0.58)$. The double layer could be visually observed only at $0.08 \leqslant x_2 \leqslant 0.25$ (dotted curve in Fig. 1) owing to the difficulties arising from the similarity of the refractive indexes of the components. The composition of the compound obviously lies within the limits of the double layer region.

As regards solutions where $0.08 \leqslant x_2 \leqslant 0.58$, owing to difficulties to obtain solid phase separation on cooling, as a rule heating curves were preferred. In the contiguous region $0.58 \leqslant x_2 \leqslant 0.8$ metastable equilibria (dashed line in Fig. 1) could be observed.

In the sulfolane richer region, the freezing points lie on two straight lines crossing at 287.2 K. This denotes the occurrence of the solid phase transition: plastic phase I → crystalline phase II[8]. However, the temperature appears to be a little lower

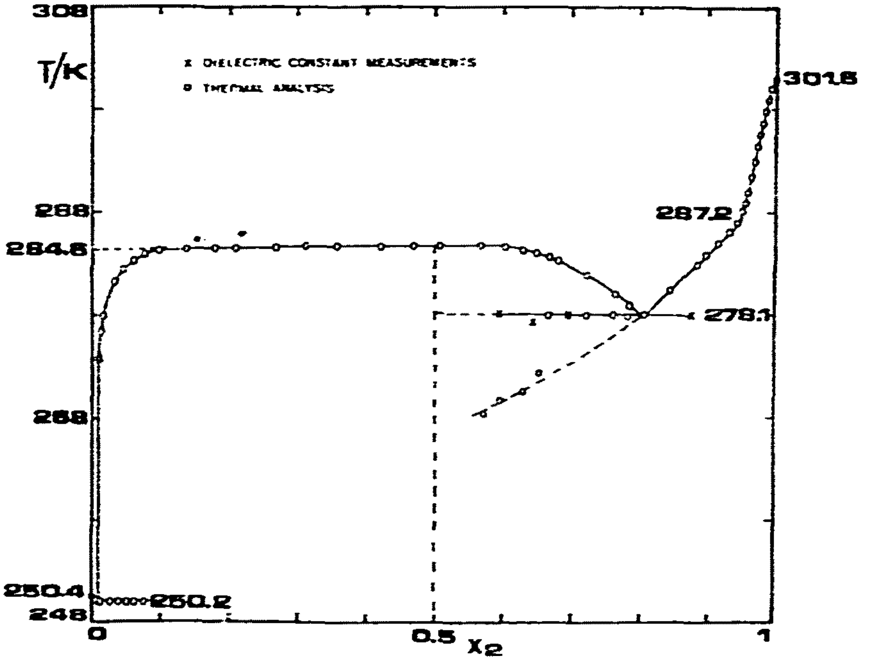

Fig. 1. Phase diagram for carbon tetrachloride(1) + sulfolane(2).

TABLE 1

FREEZING TEMPERATURES, T_f, OF MIXTURES OF CARBON TETRACHLORIDE(1)+SULFOLANE(2)

x_2	T_f (K)	T_f (K)	T_E (K)	x_2	T_f (K)	T_E (K)
0.0	250.36	—	—	0.6729	283.77	277.98
0.0110	250.34	—	—	0.6832	283.39	—
0.0117	273.64	—	250.21	0.7263	282.23	277.99
0.0137	277.24	—	249.92	0.7673	280.34	277.99
0.0287	279.70	—	250.21	0.7883	279.11	278.12
0.0344	281.27	—	250.21	0.8104	—	278.12
0.0492	282.65	—	250.11	0.8461	280.53	278.11
0.0574	283.24	—	—	0.8850	282.95	—
0.0655	283.45	—	250.02	0.9024	283.91	—
0.0798	284.13	—	249.92	0.9202	285.01	—
0.1045	284.32	—	—	0.9371	286.40	—
0.1433	284.52	—	—	0.9458	287.01	—
0.1809	284.54	—	—	0.9551	288.45	—
0.2090	284.59	—	—	0.9570	289.08	—
0.2679	284.62	—	—	0.9604	290.10	—
0.3160	284.69	—	—	0.9653	291.56	—
0.3580	284.67	—	—	0.9702	292.99	—
0.4295	284.74	—	—	0.9752	294.45	—
0.4669	284.77	—	—	0.9793	295.58	—
0.5114	284.79	—	—	0.9828	296.61	—
0.5712	284.76	—	—	0.9879	298.08	—
0.5735	284.30	268.68	—	0.9921	299.31	—
0.6021	284.18	269.86	—	0.9943	299.95	—
0.6337	284.06	270.58	—	0.9965	300.58	—
0.6505	283.98	—	—	0.9996	301.47	—
0.6554	—	272.72	—	1.0	301.60	—

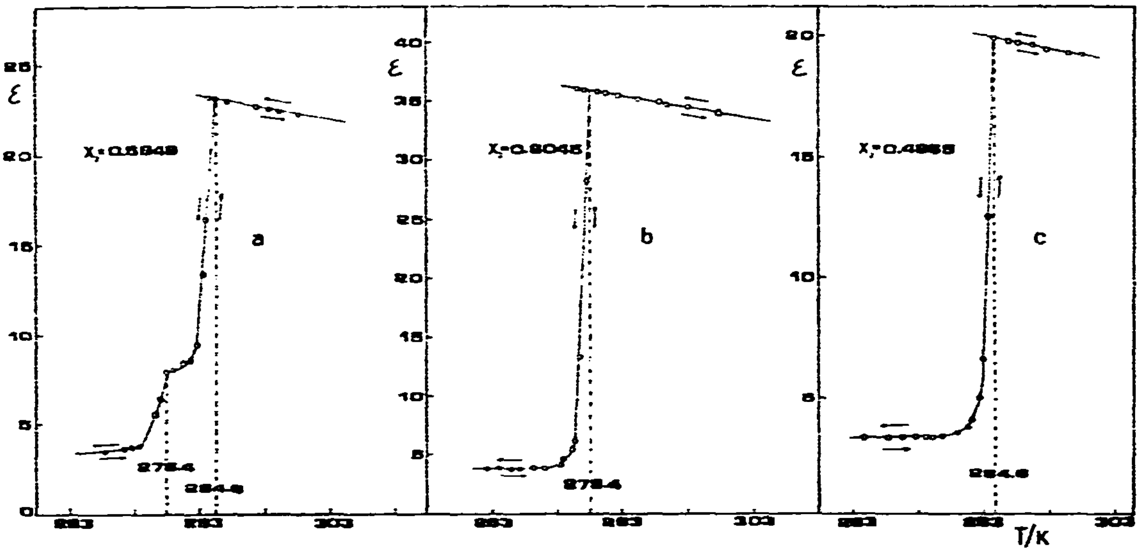

Fig. 2. Dielectric constant–temperature curves in a temperature range including phase transition.

with respect to the transition temperature of pure sulfolane (288.6 K), thus supporting the assumption that sulfolane and carbon tetrachloride form plastic mixed crystals, in agreement with the fact that both components have similar "globular" molecules.

Thermal data are supported by some dielectric constant measurements covering a wide temperature range including phase transitions, with the exception of the eutectic halt at 250.2 K. Dielectric constant temperature plots (Fig. 2) show two continuous transitions ending at 278.4 K (eutectic halt) and at 284.6 K (incongruent melting point of the compound); the former is lacking in the region 0.1 to 0.5 x_2 and becomes steeper the more the worked mixture approaches eutectic composition ($x_2 = 0.8$) (curves a and b), whereas the latter is sharper at 0.5 x_2 (curve c).

It would be reasonable to assume that molecules in the solid phase gain some rotational freedom on heating, due to a cooperative process culminating at the transition temperatures and can only freely rotate in the liquid phase.

The sharpness of the transition at 0.5 x_2, as well as the evidence of the eutectic halt, by dielectric and thermal measurements, only for mole fractions higher than 0.5, clearly indicate that the ratio 1:1 is the likely composition of the incongruently melting compound. The same molecular ratio arises from direct analysis of melts deriving from the solid phase separated, by filtering, at a temperature not far from 284 K starting from solutions whose composition covered the region 0.3 to 0.6 x_2; the composition of melts approaches 0.5 x_2 from both sides of the worked composition range.

Dielectric constants of liquid mixtures

The dielectric constants $\varepsilon_{1,2}$ show negative deviations of measured values at 303.15, 313.15 and 323.15 K with respect to ideal values calculated on the basis of a rectilinear dependence of dielectric constants on the ideal volume fraction, ϕ_2, of sulfolane, in the mixture. In Fig. 3, $\varepsilon_{1,2}$ values, at 313.15 K, are plotted against ϕ_2 (curve a) together with the deviations $\varepsilon^E_{1,2}$ which show a minimum slightly shifted towards the CCl_4 richer region which becomes less noticeable with increasing temperature. Such a temperature effect was not observed in the case of the sulfolane + benzene system[5], where no intermediate compound was detectable.

In Table 2 are summarized values of x_2, $\varepsilon_{1,2}$ and the apparent dielectric constants of sulfolane $\bar{\varepsilon}_2$, calculated as $\bar{\varepsilon}_2 = (\varepsilon_{1,2} - \varepsilon_1 \phi_1)/\phi_2$. From the $\bar{\varepsilon}_2$ values the dipole moments μ_2 have been calculated by the Mecke and Reuter equation[10], in the simplified form, suitable in the case of strongly polar solutes dissolved in an inert medium.

$$\surd\mu^2 = \frac{(\bar{\varepsilon}_2 - n_2^2)(2 + n_2^2)/\varepsilon_{1,2}}{(n_2^2 + 2)^2} 9\varepsilon_0 kTV_2/L \left[1 + \frac{(\varepsilon_2 - \varepsilon_1)\varphi_1 (n_2^2 - \varepsilon_1)}{(2\varepsilon_{1,2} + \varepsilon_1)(\bar{\varepsilon}_2 - n_2^2)} \right] \tag{1}$$

In the last column of Table 2 are summarized the deviations from unity of the correlation parameter $g = \mu_2^2/\mu_0^2$ ($\mu_0 = 4.8_2$) which is the ratio of the actual molar orientation polarization of sulfolane to that in an infinitely dilute solution. Data of the $(g-1)$ term, negative in the entire composition range with a minimum in dilute solutions, exceed the values generally accepted as indicative of no noticeable interaction between molecules, but for dipole–dipole interactions[10].

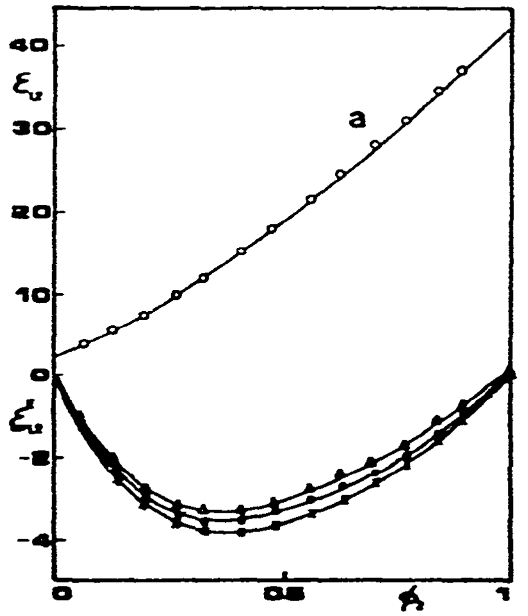

Fig. 3. Dielectric constant $\varepsilon_{1,2}$ plotted against ideal volume fraction ϕ_2. × = 303.15 K; ○ = 313.15 K △ = 323.15 K.

TABLE 2

DIELECTRIC CONSTANTS, $\varepsilon_{1,2}$, OF CARBON TETRACHLORIDE(1)+SULFOLANE(2) MIXTURES; APPARENT CONSTANTS, $\bar{\varepsilon}_2$, OF SULFOLANE AND CORRELATION PARAMETERS g

x_2	$\varepsilon_{1,2}$			$\bar{\varepsilon}_2$			$g-1$		
T (K)	*303.15*	*313.15*	*323.15*	*303.15*	*313.15*	*323.15*	*303.15*	*313.15*	*323.15*
0.0	2.218	2.198	2.178	—	—	—	—	—	—
0.0660	3.703	3.659	3.611	25.25	24.98	24.65	−0.30	−0.28	−0.25
0.1374	5.424	5.348	5.270	26.07	25.75	25.42	−0.32	−0.30	−0.28
0.2048	7.373	7.250	7.109	27.90	27.49	26.98	−0.30	−0.29	−0.26
0.2794	9.914	9.715	9.510	30.27	29.71	29.13	−0.26	−0.25	−0.23
0.3345	12.00	11.71	11.45	31.96	31.23	30.60	−0.23	−0.22	−0.20
0.4188	15.48	15.11	14.74	34.36	33.60	32.83	−0.18	−0.17	−0.16
0.4879	18.51	18.04	17.58	36.05	35.20	34.36	−0.15	−0.14	−0.12
0.5667	22.05	21.51	20.99	37.61	36.75	35.91	−0.12	−0.11	−0.09
0.6334	25.16	24.51	23.89	38.78	37.83	36.93	−0.09	−0.08	−0.07
0.7050	28.43	27.69	27.01	39.68	38.69	37.79	−0.08	−0.07	−0.05
0.7743	31.74	30.94	30.14	40.57	39.58	38.60	−0.06	−0.05	−0.03
0.8473	35.36	34.42	33.51	41.49	40.41	39.37	−0.04	−0.03	−0.01
0.8955	37.91	36.85	35.83	42.18	41.02	39.90	−0.03	−0.02	+0.01
1.0	43.38	42.12	40.71	43.38	42.12	40.71	0.00	+0.01	+0.02

Viscosities

In Table 3 measured values of the viscosity $\eta_{1,2}$ are summarized for (1)+(2) binary systems, at 303.15, 313.15 and 323.15 K. According to Eyring theory, the equation:

$$\eta = (Nh/V)\exp(-\Delta S^{\neq}/R)\exp(\Delta H^{\neq}/RT) \tag{1}$$

correlates viscosity to temperature for a pure liquid; $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are the activation enthalpy and entropy of viscous flow, V the molar volume of the pure substance, N and h the Avogadro and Planck constants, respectively. On the supposition that the viscous flow activation parameters are additive functions[11] for ideal systems, the use of eqn (1) in the form:

$$\log \eta_{1,2} V_{1,2} = x_1 \log \eta_1 V_1 + x_2 \log \eta_2 V_2 \tag{2}$$

allowed us to emphasize positive deviations from ideality for the sulfolane+carbon tetrachloride system. Equation (1) moreover predicts linear plots of $\log(\eta_{1,2} V_{1,2})$ against T^{-1}. From these plots, for all the worked mixtures, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ have been calculated and $\Delta G^{\neq}$ derived at 313.15 K (Table 3). Then excess functions $H^{\neq E}$, $S^{\neq E}$ and $G^{\neq E}$, at 313.15 K, have been calculated and plotted against composition in Fig. 4 together with the excess volumes of mixing V^E (ref. 4).

If the criterium[11,12] is accepted that positive $G^{\neq E}$ values are indicative of interactions between unlike molecules, the data in Fig. 4 do not allow preclusion of

TABLE 3

VISCOSITY AND ACTIVATION PARAMETERS, $\Delta H^{\neq}$, $\Delta S^{\neq}$, AND $\Delta G^{\neq}$ OF VISCOUS FLOW FOR CARBON TETRACHLORIDE(1)+SULFOLANE(2) MIXTURES

x_2	$\eta_{1,2}$ (*mPa s*)			$\Delta H^{\neq}$ (*cal$_{th}$ mol^{-1}*)	$\Delta S^{\neq}$ (*cal$_{th}$ K^{-1} mol^{-1}*)	$\Delta G^{\neq}$ *(313.15 K)* (*cal$_{th}$ mol^{-1}*)
	T (K)					
	303.15	*313.15*	*323.15*			
0.0	0.8438	0.7392	0.6543	2230	−3.24	3245
0.0660	1.002	0.8678	0.7607	2447	−2.85	3339
0.1374	1.243	1.062	0.9177	2727	−2.35	3463
0.2048	1.532	1.286	1.098	3026	−1.77	3580
0.3138	2.043	1.691	1.425	3303	−1.54	3785
0.3838	2.392	1.974	1.658	3371	−1.50	3841
0.4188	2.589	2.133	1.790	3405	−1.48	3868
0.4879	3.046	2.498	2.082	3521	−1.40	3959
0.5667	3.682	2.982	2.470	3712	−1.22	4094
0.6334	4.338	3.481	2.855	3904	−0.91	4189
0.7050	5.162	4.107	3.348	4052	−0.76	4290
0.7743	6.124	4.817	3.900	4239	−0.49	4392
0.8473	7.286	5.711	4.571	4390	−0.34	4496
0.8955	8.168	6.367	5.083	4472	−0.29	4563
1.0	10.295	8.007	6.346	4640	−0.19	4699

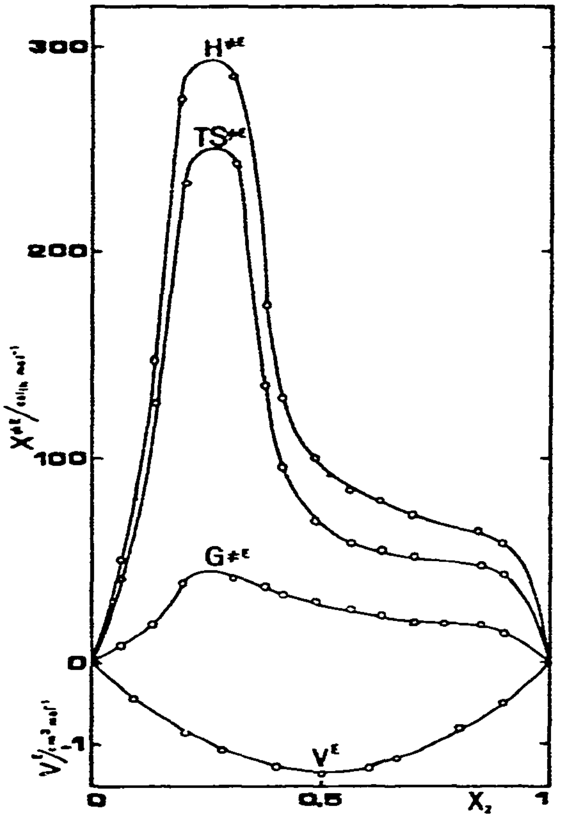

Fig. 4. Excess viscous flow activation function $X^{\neq E}$ and excess volumes V^E plotted against mole fraction x_2, at 313.15 K.

interactions between sulfolane and carbon tetrachloride. On the other hand, a feature of the $H^{\neq E}$ vs. composition curve which steeply gains a maximum, approximately at 0.3 x_2, is its asymmetric form; it may be interpreted as indicative[13] of a likely phase separation with decreasing temperature, as it is the case.

4. CONCLUSION

The main conclusion which may be drawn from collected data is that the occurrence of a 1:1 compound between sulfolane and carbon tetrachloride, which decomposes on melting, may be ascribed to a favourable crystals geometry rather than to strong specific interactions. The ability of carbon tetrachloride to form mixed crystals with plastic sulfolane, phase I, supports this assumption. On the other hand, the presence of empty 3d levels in chloride atoms and the exposed negative end of the dipole in sulfolane molecules might account for the likely, though weak, interactions which are evidenced in liquid solutions by viscosity and dielectric constant measurements.

REFERENCES

1 O. Sciacovelli, L. Jannelli and A. Della Monica, *Gazz. Chim. Ital.*, 97 (1967) 1012.
2 M. Della Monica, L. Jannelli and U. Lamanna, *J. Phys. Chem.*, 72 (1968) 1068.
3 L. Jannelli, O. Sciacovelli, A. Della Monica and A. Dell'Atti, *Proc. 1st Int. Conf. Calorimetry and Thermodynamics, Warsaw, 1969*, p. 907.
4 A. Sacco and L. Jannelli, *J. Chem. Thermodyn.*, 4 (1972) 191.
5 L. Jannelli and A. Sacco, *J. Chem. Thermodyn.*, 4 (1972) 715.
6 L. Jannelli, A. Inglese, A. Sacco and P. Ciani, *Z. Naturforsch.*, 30a (1975) 87.
7 A. Sacco and A. K. Rakshit, *J. Chem. Thermodyn.*, 7 (1975) 257.
8 J. B. Ott, J. R. Goates and A. H. Budge, *J. Phys. Chem.*, 66 (1962) 1387.
9 J. Kendal, E. D. Crittenden and H. K. Miller, *J. Amer. Chem. Soc.*, 45 (1923) 963; P. I. Fedorov, A. G. Dudareva and N. F. Drobot, *Russian J. Inorg. Chem.*, 8 (1963) 667.
10 R. Mecke and A. Reuter, *Z. Naturforsch.*, 4a (1949) 368.
11 T. M. Reed and T. E. Taylor, *J. Phys. Chem.*, 63 (1959) 58.
12 R. Meyer, M. Meyer, J. Metzger and A. Peneloux, *J. Chim. Phys.*, 68 (1971) 406.
13 C. G. Savini, D. R. Winterhalter and H. C. Van Ness, *J. Chem. Eng. Data*, 10 (1965) 171; E. T. Chang and E. F. Westrum, *J. Phys. Chem.*, 69 (1965) 2176; R. H. Stokes and C. Burfitt, *J. Chem. Thermodyn.*, 5 (1973) 623.