methyl alcohol from the chloride is larger.) These were excluded from the average. The average value of $\lambda_0(LK^+)$ is $45.5_5 \pm 1.4$ in AN, 55.5 ± 1.4 in AC, 6.33 ± 0.31 in PC, 18.7 ± 0.2 in DMF, 27.74 ± 0.13 in MeOH, 8.21 ± 0.59 in *i*-PrOH, and 5.80 ± 0.37 in *n*-BuOH.

The last two columns of Table I list the association constant, $K_A(LKX)$, and the so-called "center-to-center distance of closest approach" (in angstroms), $a(LKX)$, of LK^+ and LK^+ and X^- in the ion pair as calculated from the Fuoss-Hsia treatment.

Mobility of K^+. The mobility of K^+ at infinite dilution has been reported to be 83.6 in AN (*16*), 11.17 in PC (*17*), 30.8 in DMF (*18*), and 52.45 in MeOH (*19*). As values of $\lambda_0(K^+)$ in *i*-PrOH and *n*-BuOH were not available, they were estimated in the present work from conductance data of tetraethylammonium and potassium dichloropicrates. Unlike potassium picrate, which has a low solubility, potassium dichloropicrate is soluble to at least 0.02 M in these alcohols. Since $\lambda_0\ (Pi^-)$ has not been reported in *n*-BuOH, the conductivity of solutions of tetraethylammonium picrate has been measured in this solvent. From a Fuoss and Kraus treatment of less precise conductance data (±1%) the following values of Λ_0 and K_A were obtained: Et_4NPiCl_2 ($PiCl_2^-$ = dichloropicrate), 27.0, $7.3_2 \times 10^2$ in *i*-PrOH and 18.7_1, $1.0_8 \times 10^3$ in *n*-BuOH; $KPiCl_2$, 22.5, $1.0_2 \times 10^3$ in *i*-PrOH and 17.9_8, $1.7_2 \times 10^3$ in *n*-BuOH; Et_4NPi, 19.5_8 and $8.3_1 \times 10^2$, respectively, in *n*-BuOH. From Λ_0 of Et_4NPiCl_2, $KPiCl_2$, and Et_4NPi and $\lambda_0(Et_4N^+) = 14.6_8$ in *i*-PrOH (*20*) and 10.40 in *n*-BuOH (*21*), $\lambda_0(K^+) = 10.1_8$ and 9.6_7 in *i*-PrOH and in *n*-BuOH, respectively, while $\lambda_0(Pi^-) = 9.1_8$ in *n*-BuOH.

Discussion

From the average values of $\lambda_0(LK^+)$ and $\lambda_0(K^+)$ presented in the Results section, the ratio $\lambda_0(LK^+)/\lambda_0(K^+)$ is found to be equal to 0.54_5 in AN, 0.56_5 in PC, 0.61 in DMF, 0.53 in MeOH, 0.81 in *i*-PrOH, and 0.60 in *n*-BuOH. The markedly decreased mobility of LK^+ as compared to that of K^+ must be ascribed to partial replacement of the solvation layer(s) around K^+ by the bulky ligand. This effect, which varies with the solvent, is promoted by screening of the charge on K^+ in LK^+ as a consequence of binding to the six oxygens of the crown. Takeda (*22*) arrived at the same conclusion for the 18-crown-6 K^+ complex salt in DMF. The reduction in ion mobility is less when potassium is complexed with the less bulky 18-crown-6 and dibenzo-18-crown-6 ligands than with di-*tert*-butyldibenzo-18-crown-6. The ratio $\lambda_0(18\text{-cr-}6\ K^+)/\lambda_0(K^+) = 8.91/11.1_7 = 0.80$ in PC (*23*) and $24.6/30.8 = 0.80$ in DMF (*22*), while in PC $\lambda_0(DB\text{-}18\text{-cr-}6\ K^+)/\lambda_0(K^+)$ derived from the perchlorate salt is $(25.80\ (24) - 18.44\ (17))/11.1_7 = 0.66$. In methyl alcohol this ratio is equal to $32.9/52.4_5 = 0.62_6$ (*25*).

The solvodynamic radius of LK^+ in the various solvents cannot be calculated by using the Stokes-Einstein equation, considering the nonspherical nature of the *tert*-butylbenzo crown ether (the same is true for dibenzo-18-crown-6). However, it may be noted that the average value of $\lambda_0(LK^+)\eta$ of $0.15_5 \pm 0.2$ (Table I) is comparable to that of *n*-heptylammonium ion in many solvents.

The relation between solvated and contact ion pairs on the one hand and the values of *a* will be discussed in a subsequent paper.

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Received for review May 3, 1982. Accepted January 25, 1983. G.R. acknowledges financial support from the Fonds National de la Recherche Scientifique and the Institut Interuniversitaire des Sciences Nucléaires de Belgique. I.M.K. thanks the National Science Foundation for Grant CHE-8000243 for support of this work.

Hydrogen Solubility in Organic Liquids

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The solubility of hydrogen was measured in α-methylstyrene, cumene, cyclohexene, cyclohexane, and cyclohexanone at temperatures between 30 and 100 °C and pressures between 100 and 1000 psig. Henry's constants calculated from the solubility data were correlated as a function of temperature.

The hydrogen solubility in organic liquids is needed in the analysis and design of multiphase reactors. Hydrogen solubility data at high temperature and pressure are rather limited (*1*). Most of the data were measured near room temperature and atmospheric pressure (*2*).

The purpose of this study is to determine the solubility of hydrogen in organic liquids by a simple and accurate method. The liquids α-methylstyrene, cumene, cyclohexene, cyclohexane, and cyclohexanone were studied. Solubility measurements in α-methylstyrene reported in the literature (*3*, *4*) indicate large discrepancies. Berty et al. (*5*) published a com-

0021-9568/83/1728-0164$01.50/0

Table I. Solubility Data and Calculated H and $\Delta\overline{H}_s$

compd	temp, °C	$10^{-3}H$, atm	10^3X_H					$\Delta\overline{H}_s$, kcal/(g-mol)
			100 psig	300 psig	500 psig	800 psig	1000 psig	
α-methylstyrene	30	3.25	2.39	6.55	10.8	17.1	21.2	1.18
	60	2.72	2.84	7.88	12.9	20.3	25.4	
	100	2.25	3.36	9.45	15.5	24.7	30.4	
cumene	60	2.13	3.44	10.2	16.7	26.0	32.4	1.33
	100	1.72	4.15	12.5	20.5	32.7	39.7	
cyclohexene	30	3.06	2.38	7.02	11.5	17.8	22.5	1.49
	100	1.92	3.03	10.3	17.6	28.0	34.9	
cyclohexane	30	2.74	2.73	7.69	12.7	20.2	24.8	1.35
	60	2.22	3.11	9.40	15.9	25.8	29.3[a]	
	100	1.80	3.20	11.2	18.6	29.9	36.8[b]	
cyclohexanone	30	4.52	1.58	4.72	7.87	12.4	15.1	1.49
	60	3.54	2.03	6.15	10.1	15.7	18.5[a]	
	100	2.80	2.63	7.48	12.5	20.0	24.3	

[a] $P = 950$ psig. [b] $P = 980$ psig.

prehensive study on the hydrogen-cyclohexane system which included solubility data over a wide range of temperatures (37-138 °C) and pressures (34-376 atm).

Experimental Section

The solubility apparatus consists of a high-pressure 0.75-gal autoclave manufactured by Autoclave Engineers and a gas measuring train. A detailed description of the apparatus and operation has been reported previously (*6*). The solubility train includes two gas burets (100- and 600-cm^3 volume) connected to a liquid sample buret (50 cm^3). The burets are jacketted so as to control their temperature to ±0.1 °C.

The purity of the liquids, as stated by the manufacturers (Aldrich and Merck Co.), was better than 99%.

Preliminary experiments were carried out to test the approach to equilibrium by increasing the pressure or the temperature in the equilibrium cell to a certain value or by decreasing them to the same temperature and pressure. Good agreement was obtained between the solubility measured by both experimental methods, indicating that true equilibrium was achieved.

Results and Discussion

At each temperature and pressure, three or four measurements of the gas volume flashed from a volume of liquid were carried out. The difference between the ratios of the two volumes was less than 3%. The average value of these ratios was converted to an apparent mole fraction of hydrogen in the liquid as follows:

$$x'_H = \frac{(V_g/V_L)\left[\dfrac{(P_1 - P_v)}{RT_1}\dfrac{M_w}{\rho_L}\right]}{1 + (V_g/V_L)\left[\dfrac{P_1 - P_v}{RT_1}\dfrac{M_w}{\rho_L}\right]} \tag{1}$$

where V_g and V_L are the gas and liquid volumes, respectively. P_v and ρ_L are the liquid vapor pressure and density at the temperature T_1 and pressure P_1 in the solubility train. M_w is the molecular weight of the liquid.

The mole fraction of hydrogen in the liquid, x_H, is the sum of the apparent mole fraction x'_H and the mole fraction of hydrogen, x''_H, dissolved in the liquid after equilibrium in the solubility train was reached. When the solubility is small, x_H is related to the fugacity of the hydrogen in the gas phase according to Henry's law

$$f_H = Hx_H \tag{2}$$

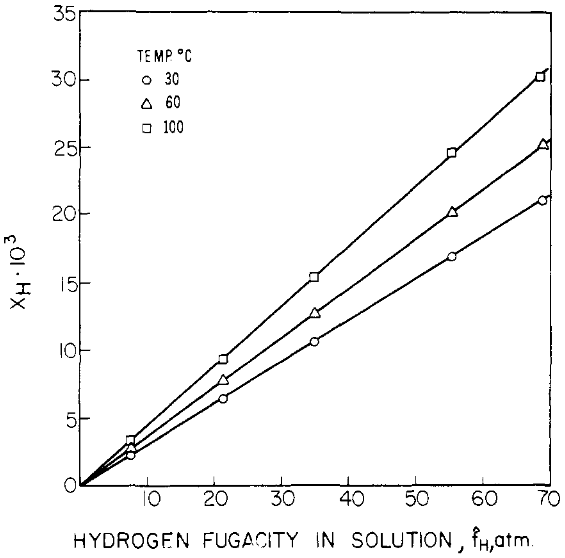

Figure 1. Solubility of hydrogen in α-methylstyrene.

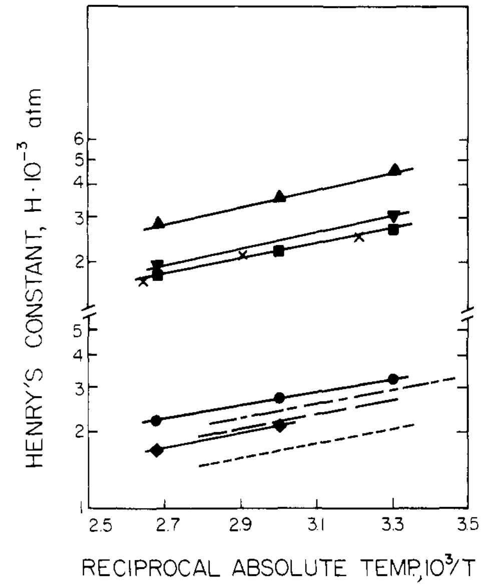

Figure 2. Effect of temperature on Henry's constant: (■) cyclohexane, (▼) cyclohexene, (●) α-methylstyrene, (♦) cumene, (▲) cyclohexanone, (—— ——) α-methylstyrene (Stefoglo et al. (*4*)), (- - -) cumene (Stefoglo et al. (*4*)), (—— - ——) α-methylstyrene (Herskowitz et al. (*3*)), (X) cyclohexane (Berty et al. (*5*)).

The fugacity of hydrogen was calculated from the data of Michels et al. (*7*), assuming that the gas phase is pure hydrogen.

A linear least-squares analysis yielded values of H and x''_H at each temperature. The values of x_H and H are listed in Table

I. A plot of x_H vs. f_H for the hydrogen–α-methylstyrene system is shown in Figure 1.

The Henry's law constant may be expressed as a function of temperature as follows (*1*):

$$\ln H = \Delta \bar{H}_s / RT \tag{3}$$

where $\Delta \bar{H}_s$ is the molar heat of solution. *H* is plotted as a function of temperature in Figure 2. The calculated values of $\Delta \bar{H}_s$ from this plot are listed in Table I.

For comparison *H* values calculated from solubility data published in the literature are also plotted in Figure 2. The agreement with the Berty et al. (*6*) data is excellent. A good agreement with the Herskowitz et al. (*3*) data is observed. On the other hand, the results published by Stefoglo et al. (*4*) for both α-methylstyrene and cumene are considerably lower.

Registry No. Hydrogen, 1333-74-0; α-methylstyrene, 98-83-9; cumene, 98-82-8; cyclohexene, 110-83-8; cyclohexane, 110-82-7; cyclohexanone, 108-94-1.

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Received for review March 10, 1982. Accepted November 15, 1982.

Thermodynamic and Physical Properties of Binary Mixtures Involving Sulfolane. 2. Excess Dielectric Constants on Mixing Sulfolane + Propionitrile, + Butyronitrile, + Valeronitrile

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Dielectric constants were measured for three binary systems involving sulfolane + propionitrile, + butyronitrile, and + valeronitrile, over the entire composition range, at selected temperatures ranging between 293.16 and 333.16 K. The behavior of excess dielectric constant vs. composition plots markedly differentiates each system with respect to others; it is however indicative of only moderate interactions of any kind, mainly dipole–dipole interactions, whose importance decreases in a fashion consistent with the diminished role of polarity with lengthening nitrile carbon chain. Data strongly substantiate the supposition that self-association of nitrile to molecular pairs predominates with respect to nitrile–sulfolane interactions with increasing temperature and nitrile chain length, in accord with our previous interpretation of excess volume data.

Introduction

Previous data (*1*) on excess volumes on mixing sulfolane + propionitrile, + butyronitrile, and + valeronitrile were interpreted in terms of moderate competitive interactions between like and unlike molecules, mainly dipole–dipole interactions, whose importance steadily decreases with increasing nitirile chain length (in spite of a dipole moment (μ = 3.57 D) unaffected by molecular size, the polarity indeed plays obviously a reduced role with lengthening nitrile carbon chain). Nevertheless, with increasing temperature self-association of nitrile seems to predominate with respect to interactions with sulfolane according to the observed increased volume contractions on mixing; and this according to the supposition of a more compact structure can be ascribed to the nitrile self-association product rather than to the complex with sulfolane, because of the steric hindrance of its globular molecule.

In order to better substantiate the above interpretation we carried out measurements of dielectric constants of the three binary systems, over the entire composition range, at selected temperatures ranging between 293.16 and 333.16 K.

Table I. Dielectric Constants for Pure Components, ϵ°, Parameters *A, B, C, D,* and Standard Deviations σ of the Smoothing Equations

T/K	ϵ°_1	ϵ°_2	A'	B'	C'	D'	σ
		Propionitrile (1) + Sulfolane (2)					
293.16	28.86	[44.62]	2.994	−0.764	0.932		0.02
303.16	27.59	43.38	2.778	−1.084	1.105		0.02
313.16	26.48	42.14	2.632	−1.487	1.229		0.02
		Butyronitrile (1) + Sulfolane (2)					
293.16	24.83	[44.62]	0.692	−0.868	0.721	1.054	0.02
303.16	23.73	43.41	0.467	−0.808	1.072		0.02
313.16	22.79	42.15	0.444	−1.058	1.006		0.02
333.16	20.83	39.83	0.648	−0.841	0.845	−0.634	0.04
		Valeronitrile (1) + Sulfolane (2)					
303.16	19.39	43.38	−2.266	−1.023	0.099		0.02
313.16	18.64	42.14	−2.253	−1.001	0.973		0.03
323.16	17.89	40.94	−2.240	−1.134	1.763		0.04
333.16	17.14	39.84	−1.926	−1.334	2.705		0.04

Experimental Section

Materials, Apparatus, and Procedure. Sulfolane, kindly supplied by Shell Italia, was purified and dried as already reported (*2*); the melting point of the final product was 301.61 K, in close agreement with our own previous data and the most reliable literature data (*3*); BDH nitriles were purified and dried as already (*4*) reported.

Solutions were made by weight (reduced to mass), stored in dark containers, and protected from moisture as far as possible.

The apparatus for measuring dielectric constants was described elsewhere (*5*); the error in the dielectric constants was estimated to be 0.04ϵ.

Dielectric constants were measured over the entire composition range; working temperatures were 293.16, 303.16, and 313.16 K in the case of propionitrile + sulfolane, 293.16, 303.16, 313.16, and 333.16 K in the case of butyronitrile +

0021-9568/83/1728-0166$01.50/0