326 *J. Chem. Eng. Data* **1993**, *38*, 326-327

Solubility of 2,3-Dimethyl-2,3-dinitrobutane

Marek E. Krzymien

Institute for Aerospace Research, National Research Council, Ottawa, Canada K1A 0R6

The solubility of 2,3-dimethyl-2,3-dinitrobutane (DMNB) in acetone, acetonitrile, benzene, cyclohexanone, *N,N*-dimethylformamide, dimethyl sulfoxide, 1,4-dioxane, 2-ethoxyethanol, ethyl acetate, hexane, methanol, methyl ethyl ketone, tetrahydrofuran, toluene, and water at 5, 15, 25, and 35 °C has been determined. The concentration of DMNB was measured by capillary gas chromatography with electron capture detection. The relative standard deviation of the measurements was between about 1% and 7%.

Introduction

2,3-Dimethyl-2,3-dinitrobutane (DMNB) is a relatively little known compound with only a few references in the open literature. It seems to have had only one potential industrial application as a combustion-improving additive to diesel fuel (*1*). In chemical research it has found a few applications as a model compound (*2, 3*). Not many of its physical properties are readily available. Until now DMNB solubility has been only inferred from its chemical structure, and no quantitative data are available. The compound is of interest because it has a high electron capture detector response and it is amenable to the analysis by gas chromatography. These features make it useful as an internal standard and/or as a potential marking agent for identifying certain industrial materials when added to them in minor quantities.

In this connection, the development of a method for determination of DMNB in solid mixtures (*4*) required a detailed knowledge of its solubility in many solvents. Acetone, acetonitrile, benzene, cyclohexanone, *N,N*-dimethylformamide, dimethyl sulfoxide, 1,4-dioxane (dioxane), 2-ethoxyethanol, ethyl acetate, hexane, methanol, methyl ethyl ketone, tetrahydrofuran, toluene, and water were studied as possible candidates for selective extraction of DMNB from a solid matrix. The solubility of DMNB in these solvents at 5, 15, 25, and 35 °C has been determined and is reported here.

Experimental Section

Materials. Distilled-in-glass (minimum 99.5% purity) solvents used in the project were supplied by Caledon Laboratories Ltd. DMNB (98% purity) was purchased from Aldrich Chemical Co. and was used as received.

Procedure. Approximately 5 g of DMNB was placed in 25-mL Reacti-Flasks, and 25 mL of solvent was added. The flasks were closed with Teflon-lined septa and screw caps, shaken well, and placed in a constant-temperature bath. The contents of the flasks were frequently shaken to speed the dissolution and ensure uniform concentration. After a week at a given temperature a 100-μL sample of the solution was withdrawn with a syringe and diluted to 25 mL with acetone. This stock solution was further diluted with hexane in a ratio dependent on its concentration, suitable for gas chromatographic analysis. The concentration of the solution injected into the gas chromatograph was between 3 and 100 pg/μL.

The water bath temperature was initially maintained at 35 °C and then lowered to 25, 15, and eventually 5 ± 0.01 °C. When the solution saturated at 35 °C was sampled, the syringe was preheated to about 36 °C to prevent the precipitation of DMNB.

GC Analysis. A Varian 4600 gas chromatograph (GC) with a Vista 401 data station was used throughout the project. The GC was fitted with an electron capture detector (ECD) and a 30 m × 0.32 mm, 0.25-μm-d_f (film thickness), SPB-5 fused silica column. The carrier gas was hydrogen at a linear velocity of 53 cm/s. Nitrogen at a flow rate of 30 cm^3/min was the ECD makeup gas. The oven temperature was initially 100 °C for 1 min, increased at a rate of 5 °C/min to a final temperature of 110 °C, and held for 1 min. Injector and detector temperatures were 180 °C.

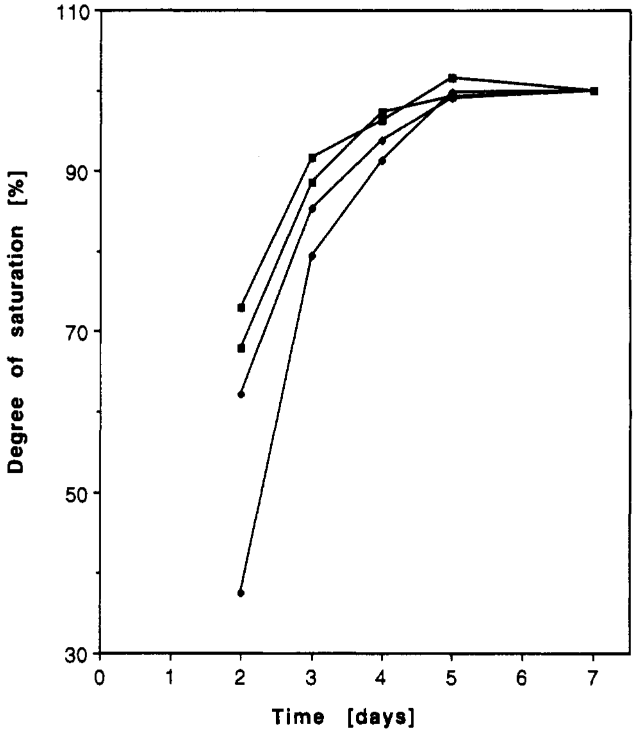

Figure 1. Time required for saturation of DMNB solution in hexane (◆), benzene (□), dioxane (◇), and dimethylformamide (■) at 35 °C.

The instrument was calibrated by the external standard method. Aliquots (1 μL) of DMNB standard solutions at concentrations of 1×10^{-11}, 2×10^{-11}, 4×10^{-11}, 6×10^{-11}, 8×10^{-11}, and 1×10^{-10} g/μL were repeatedly injected to determine the calibration factor. The calibration was checked every few days by injecting a standard solution.

Results and Discussion

Equilibration Time and Sampling. The flasks containing DMNB crystals and a solvent were first heated to 35 °C. After a week of equilibration and withdrawing samples, the bath temperature was lowered to 25 °C. After another

0021-9568/93/1738-0326$04.00/0 Published 1993 by the American Chemical Society

Table I. Concentration of Saturated Solutions of DMNB

	t = 5 °C			t = 15 °C			t = 25 °C			t = 35 °C		
solvent	determined (g/100 mL[a])	average (g/100 mL[a])	RSD (%)	determined (g/100 mL[a])	average (g/100 mL[a])	RSD (%)	determined (g/100 mL[a])	average (g/100 mL[a])	RSD (%)	determined (g/100 mL[b])	average (g/100 mL[b])	RSD (%)
acetone	7.12	7.10	2.62	9.31	9.66	4.54	14.14	13.98	1.00	17.45	18.24	3.92
	6.90			10.15			13.96			18.85		
	7.27			9.51			13.85			18.41		
acetonitrile	8.22	8.23	2.07	11.85	11.81	1.27	14.87	15.10	1.84	21.41	22.70	4.96
	8.07			11.93			15.35			23.49		
	8.41			11.64			15.35			23.20		
benzene	1.81	1.74	3.83	2.53	2.41	5.81	4.26	4.31	4.87	7.81	8.05	3.34
	1.68			2.45			4.12			8.00		
	1.72			2.26			4.54			8.34		
cyclohexanone	6.58	6.89	4.06	9.51	8.87	6.28	12.63	12.19	4.35	16.33	16.04	1.56
	7.13			8.55			11.60			15.92		
	6.96			8.54			12.33			15.87		
DMF	11.32	11.62	2.28	14.13	13.38	6.26	17.75	18.31	4.20	28.44	27.67	2.53
	11.70			12.48			18.00			27.50		
	11.83			13.53			19.19			27.06		
DMSO	solution solid at this temperature			8.44	8.46	5.08	12.63	13.28	4.93	21.91	21.48	1.73
				8.04			13.28			21.31		
				8.89			13.94			21.23		
dioxane	solution solid at this temperature			6.36	6.01	6.66	9.04	8.84	4.22	15.04	14.87	1.92
				6.11			8.41			15.03		
				5.57			9.07			14.54		
ETHE	1.26	1.26	5.56	1.79	1.89	4.62	2.92	2.93	3.07	4.15	4.14	0.73
	1.33			1.96			3.02			4.17		
	1.19			1.91			2.84			4.11		
ethyl acetate	3.71	3.85	3.43	4.90	4.87	2.02	6.68	6.64	4.07	9.49	9.81	5.21
	3.97			4.95			6.89			9.54		
	3.88			4.76			6.36			10.40		
hexane	0.052	0.050	4.00	0.082	0.087	5.27	0.203	0.188	6.94	0.231	0.235	3.40
	0.048			0.088			0.184			0.245		
	0.049			0.091			0.178			0.230		
methanol	0.86	0.89	3.37	1.16	1.15	0.87	1.49	1.51	3.77	2.41	2.46	2.03
	0.91			1.15			1.57			2.46		
	0.91			1.14			1.46			2.51		
MEK	6.19	6.12	1.80	9.05	9.35	4.39	11.87	11.97	5.35	15.07	15.10	1.85
	5.99			9.18			11.39			15.39		
	6.18			9.82			12.65			14.84		
THF	5.50	5.63	0.26	8.98	9.00	1.62	11.08	11.38	5.47	14.82	15.00	2.84
	5.81			8.86			12.10			14.70		
	5.57			9.15			10.97			15.49		
toluene	1.40	1.32	7.04	1.74	1.67	3.93	3.43	3.45	3.51	4.66	4.69	1.49
	1.22			1.66			3.58			4.64		
	1.35			1.61			3.34			4.77		
water	0.005	0.005	11.55	0.007	0.007	14.29	0.012	0.012	4.81	0.017	0.016	6.25
	0.005			0.006			0.013			0.015		
	0.004			0.008			0.012			0.016		

[a] Volume of solution measured at 25 °C. [b] Volume of solution measured at 36 °C.

week of taking samples, the temperature was lowered to 15 °C and eventually to 5 °C. Only at the initial temperature of 35 °C, the time required for establishing the equilibrium between the solid and its saturated solution depended on the dissolution rate. At the lower temperatures the saturation was achieved through precipitation of the excess DMNB.

The time required for saturation of DMNB solutions in benzene, dioxane, *N*,*N*-dimethylformamide, and hexane was determined by sampling and analysis of the solutions after 2, 3, 4, 5, and 7 days at 35 °C. After 3 days the concentrations reached 80–90% of the maximum concentrations measured after 7 days. From the fifth day there was virtually no increase of concentration (Figure 1). It was therefore assumed that in 5 days the concentration reached the saturation level. The solution was allowed, however, to equilibrate at the set temperature for an additional 2 days to be absolutely certain that it was indeed saturated.

Concentration of DMNB in Saturated Solutions. The solubility of DMNB was measured in 15 common solvents. These were selected from many classes of compounds to cover a wide range of properties so the solubility in other solvents could be inferred from the present data with some credence.

1,4-Dioxane and dimethyl sulfoxide have melting points of 11.8 and 18.45 °C, respectively. The DMNB solutions in these solvents were solid at 5 °C, and no measurements were done at this temperature.

Three samples of each saturated solution were analyzed. Each value of the determined concentration presented in Table I (columns 2, 5, 8, and 11) is an average of at least three injections. The relative standard deviation of these values varies from less than 1% to about 7%. The high scatter of the values for water solutions at 5 and 15 °C was probably the result of the small numbers measured.

Acknowledgment

Special appreciation is due to Dr. Lorne Elias who offered valuable advice and encouragement.

Literature Cited

(1) Tomanova-Pietrova, P. *Khim. Ind.* (*Sofia*) 1981, 304.
(2) Tan, B. G.; Chia, L. H. L.; Huang, H. H.; Kuok, M. H.; Tang, S. H. *J. Chem. Soc.*, *Perkin Trans. 2* 1984, 1407.
(3) Fritzsche, K.; Beckhaus, H. D.; Ruechardt, C. *Chimia* 1988, *42*, 106.
(4) Krzymien, M. E. Laboratory Technical Report NRC LTR-AA6; National Research Council of Canada: Ottawa, June 1992.

Received for review September 15, 1992. Accepted December 4, 1992. The financial assistance of Transport Canada (Technical Services Branch and Security and Emergency Planning Group) is gratefully acknowledged.