Figure 1. Test of accuracy of the new proposed method. ln $(a/S)^{1/2}$ as a function of effective volume fraction of component i, Φ^*: (1) CCl_4 (1)–cyclohexane (3); (2) benzene (1)–CCl_4 (3); (3) toluene (1)–CCl_4 (3); (4) toluene (1)–benzene (3); (5) p-xylene (1)–benzene (3); (6) p-xylene (1)–toluene (3); (7) p-xylene (1)–ethylbenzene (3); (8) p-xylene (1)–cumene (3); (9) m-xylene (1)–toluene (3); (10) m-xylene (1)–cumene (3).

To further improve the theory, we employed the pseudo-two-fluid theory for the evaluation of the local volume fraction. This approach resulted in

$$\Phi_1^*/\Phi_3^* = K'K''\Phi_1/\Phi_3 \qquad (8)$$

where K' is the Purkayastha and Walkley constant and $K'' = \delta_3^{*2}/\delta_1^{*2}$. Again, $\Phi_1^* + \Phi_3^* = 1$. With such local volume fractions, we were able to obtain good predictions even in such solvents as benzene–CCl_4 and toluene–CCl_4.

Using eq 8 to define Φ_1^* and using eq 6 to evaluate δ_m, one can easily show that eq 3 can be reformulated to require a linear relationship to exist between $[\ln (a_2/S)]^{1/2}$ and Φ_1^*. In Figure 1, such a linearity is seen to exist for each of the 10 systems considered.

The method can be easily extended to any multicomponent solvent system. For each pair of the solvent components in the mixed solvent, we write an equation similar to eq 8

$$\Phi_i^*/\Phi_j^* = K'_{ij}K''_{ij}\Phi_i/\Phi_j$$

The set of equations in combination with the requirement $\sum_k \Phi_k^* = 1$ (the summation is taken only over the solvent compounds) enable us to evaluate the local volume fraction for each solvent component. These values define then δ_m (see eq 6), which in turn, when substituted into eq 3, yields the solubility of the solute in a solvent of any composition.

The method was employed for two three-component solvent systems (Table II). The three procedures used in the evaluation, the one based on eq 5 and the other two on eq 6 in combination with eq 7 and 8, respectively, yield equally good results for the p-xylene–benzene–toluene mixed solvent system. The three procedures, however, provide different results for the toluene–benzene–CCl_4 system. Only the local volume fractions defined by eq 8 give results in agreement with experiment. The different behavior of the two three-component solvent systems is due to the fact that the first system contains solvent components of practically equal abilities to complex while, in the other system, CCl_4 does not complex at all.

The modified procedure has also been tested for naphthalene in various solvents. The results are equally good if not better than for iodine.

Registry No. I_2, 7553-56-2; CCl_4, 56-23-5; cyclohexane, 110-82-7; benzene, 71-43-2; toluene, 108-88-3; p-xylene, 106-42-3; ethylbenzene, 100-41-4; cumene, 98-82-8; m-xylene, 108-38-3; n-hexadecane, 544-76-3; n-heptane, 142-82-5; isooctane, 26635-64-3.

Literature Cited

(1) Hildebrand, J. H.; Prausnitz, J. M.; Scott, R. L. "Regular and Related Solutions"; Van Nostrand-Reinhold: New York, 1970.
(2) Hildebrand, J. H.; Scott, R. L. "The Solubility of Non-Electrolytes", 3rd ed.; Dover Publications: New York, 1964; pp 202, 270.
(3) Prausnitz, J. M. "Molecular Thermodynamics of Fluid-Phase Equilibria"; Prentice-Hall: Englewood Cliffs, NJ, 1969.
(4) O'Connell, J. P.; Prausnitz, J. M. Ind. Eng. Chem. Fundam. 1964, 3, 347.
(5) Purkayastha, A.; Walkley, J. Can. J. Chem. 1972, 50, 834.
(6) Nitta, T.; Katayama, T. J. Chem. Eng. Jpn. 1974, 7, 310.
(7) Nitta, T.; Katayama, T. J. Chem. Eng. Jpn. 1975, 8, 175.
(8) Bertrand, G. L. J. Phys. Chem. 1975, 79, 48.
(9) Acree, W. E., Jr.; Bertrand, G. L. J. Phys. Chem. 1977, 81, 1170.
(10) Taylor, E. L.; Bertrand, G. L. J. Solution Chem. 1974, 3, 479.
(11) Burchfield, T. E.; Bertrand, G. L. J. Solution Chem. 1975, 4, 205.
(12) Kehiaian, H. Bull. Acad. Pol. Sci. 1965, 13, 425.
(13) Jiang, C.-Z.; Hsu, F.-J.; Fried, V. J. Chem. Eng. Data, preceding paper in this issue.
(14) Wood, S. E.; Fine, B. D.; Isaacson, L. M. J. Phys. Chem. 1957, 61, 1605.

Solubility of Trioxane in Some Common Solvents

Mohan L. Sagu,* J. Swarup, Krishna M. Sharan, and Kshitindra K. Bhattacharyya

Indian Institute of Petroleum, Dehra Dun-248 005, India

Solubility of trioxane in 11 solvents was measured at different temperatures; dichloromethane was found to be the best solvent. These solubility curves were compared with the ideal solubility curve deduced purely from thermodynamical calculations. The deviation between these two may be due to solute–solvent interaction. The heats of solution were calculated and reported.

Extraction of trioxane by a solvent, immiscible in water, is an important step for the production of trioxane. Information available on the solubility of trioxane in different solvents is scanty. Walker (1) reported the solubility in solvents like acetic acid, benzene, toluene, and trichloroethylene. Lyobomilow et al. (2) determined the solubility in methylene chloride, n-heptane, benzene, 31.9% formaldehyde solution, and water at various temperatures. But the solubility data of trioxane in
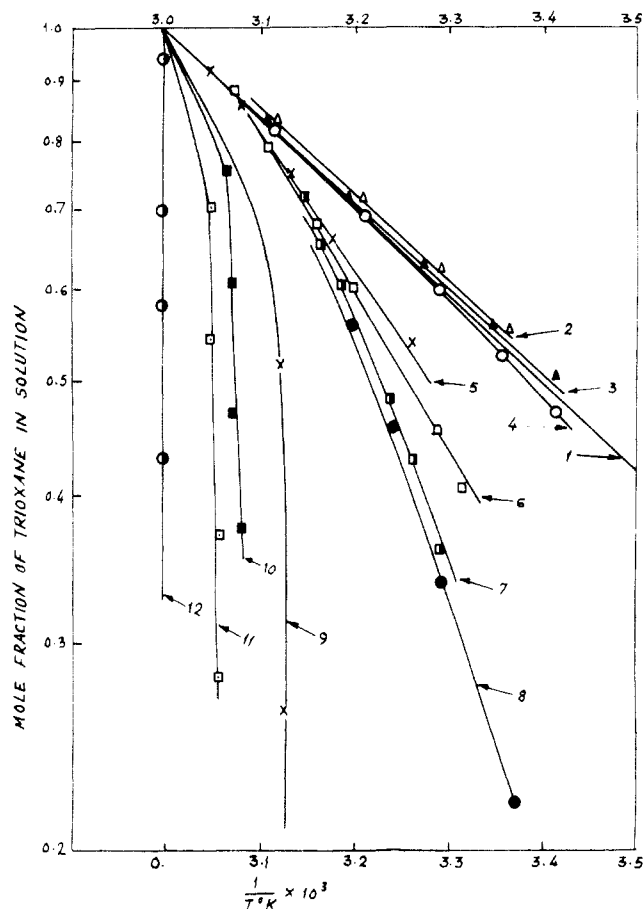
Figure 1. Solubility of trioxane in some common solvents: (1) theoretical curve, (2,△) dichloromethane, (3,▲) chloroform, (4,O) acetone, (5,X) benzene, (6,□) toluene, (7,◰) carbon tetrachloride, (8,●) methanol, (9,+) water, (10,■) cyclohexane, (11,◲) n-hexane, and 12(◑) n-cetane.

various other solvents were not reported. Solubilities of trioxane in several polar and nonpolar solvents were, therefore, determined and their behavior was compared.

Experimental Section

Trioxane was prepared in our laboratory by boiling concentrated (60%) aqueous formaldehyde solution in the presence of 10% sulfuric acid and distilling the product which contained trioxane and aqueous formaldehyde solution (3). The trioxane was extracted with methylene chloride, and this solution was further refluxed with sodium metal to remove water, if any, and the trioxane was crystallized. The water, formaldehyde, and formic acid content of trioxane was determined by the standard method of Karl Fischer (4), Tanenbaun et al. (5), and Celanese (6), respectively. AR grade solvents were used. Weighed amounts of the trioxane (about 5 g) and the solvent were taken in a well-stoppered, small glass container fitted with a thermometer pocket and a stirrer with Teflon blades. The container was immersed in a water bath and the contents were vigorously stirred. The temperature was raised slowly and near the dissolution temperature the rate of temperature rise was about 0.5 °C/min. The temperature inside was measured with an IP 15C thermometer. The temperature at which trioxane dissolved completely was first observed; then, from a higher temperature, the solution was cooled gradually and the temperature at which crystals started appearing was noted. The disappearance and the appearance of the crystals were sharp and the temperatures noted in both cases were within 0.5 °C. The average of these two temperatures was recorded against the composition of the solution. Fresh solvent was then added to increase the

Table I. Solubility of Trioxane[a]

solvent	mole fraction of trioxane in soln	soln temp, °C
dichloromethane	0.832	48.0
	0.712	39.0
	0.622	31.0
	0.553	24.5
chloroform	0.715	43.0
	0.554	27.0
	0.500	22.0
	0.455	15.5
	0.412	10.2
	0.383	6.0
acetone	0.815	49.5
	0.690	38.5
	0.597	31.5
	0.526	25.6
	0.471	20.5
benzene	0.921	55.5
	0.857	52.0
	0.749	46.5
	0.663	42.0
	0.541	34.0
toluene	0.857	54.0
	0.746	49.5
	0.665	45.0
	0.595	41.5
	0.496	36.5
	0.426	33.0
	0.331	26.0
carbon tetrachloride	0.808	52.0
	0.682	46.5
	0.589	43.0
	0.489	40.0
	0.397	36.0
	0.334	32.5
methanol	0.709	48.0
	0.548	42.0
	0.446	37.5
	0.377	34.0
	0.287	31.0
	0.194	24.0
water	0.504	48.5
	0.335	48.5
	0.251	48.0
	0.143	45.5
	0.101	41.0
	0.078	36.5
	0.063	32.0
cyclohexane	0.801	56.0
	0.572	55.0
	0.363	54.0
	0.236	52.0
	0.182	50.0
n-hexane	0.795	59.5
	0.562	57.5
	0.435	57.0
	0.338	56.5
n-cetane	0.701	61.0
	0.592	61.0
	0.431	61.0

[a] Uncertainty in mole fraction, ±0.001. Uncertainty in temperature, ±0.5.

solvent ratio and the solubility temperature was noted. This procedure was repeated to note the solubility temperature at different molar concentrations with each solvent.

Results and Discussion

A semilog plot of the mole fraction of trioxane in solution against the inverse of absolute temperature is shown in Figure 1 and the results are shown in Table I.

The solubility values in benzene, methylene chloride, and water are in agreement with the data reported by Lyobomilow et al. (2).

Table II. Heats of Solution of Trioxane in Different Solvents

solvent	10^2- (slope)	ΔH_{sol},[a] kJ/mol	ΔH_{sol} – ΔH_{fusion} kJ/mol
dichloromethane	7.3	14.0	−0.2
chloroform	7.1	13.6	−0.6
acetone	7.7	14.8	+0.6
benzene	11.8	22.7	+8.5
toluene	13.4	25.8	+11.6
carbon tetrachloride	24.0	46.1	+31.9
methanol	24.0	46.1	+31.9

[a] Heat of solution.

In ideal solution, the solubility of trioxane would be given by (7)

$$\log x = (\Delta H/2.303R)(1/T - 1/T_0) \quad (1)$$

where x = mole fraction of trioxane in solution; ΔH = 14.2 kJ/mol, the heat of fusion of trioxane (8); T_0 = 334 K, the melting point of trioxane; and R = 8.3144 J/(mol K), the gas constant.

Substituting these values

$$\log x = -742/T + 2.22 \quad (2)$$

The straight line representing eq 2 is shown as curve 1 in Figure 1. It appears that none of these solvents forms a perfectly ideal solution with trioxane. However, dichloromethane, chloroform, and acetone behave almost as ideal solvents; the deviations are negligible. In these three solvents, the heats of solution and the heat of fusion of trioxane would differ very slightly.

In higher normal paraffins like n-cetane, trioxane is almost insoluble; in lower paraffins like n-hexane, it is sparingly soluble. It is a little more soluble in cycloparaffins (e.g., cyclohexane), whereas the solubility is appreciable in methanol and carbon

tetrachloride. Among the studied solvents the solubility increases in the following order: n-cetane, n-hexane, cyclohexane, water, methanol, carbon tetrachloride, toluene, benzene, acetone, chloroform, and dichloromethane.

Trioxane is highly soluble in the aromatic hydrocarbons benzene and toluene; this is probably due to the similarity of the cyclic structures. The deviations of solubilities from the ideal solution curve 1 show that there are large solute–solvent interactions with these solvents. The slopes of curves 2 and 3 are slightly lower than that of curve 1, while the slopes of curves 4–12 are higher than that of curve 1. The heats of solution in the latter cases would, therefore, be higher than the heat of fusion. These are shown in Table II. This extra heat might possibly be consumed in interaction reactions of an endothermic nature.

It may be mentioned here that the closeness of the solubility parameters indicates the ease of solubility, so it can be inferred that such data for trioxane (11.39) and carbon tetrachloride (8.60) are far more apart than methylene chloride (9.86) and chloroform (9.30). This probably is the reason that carbon tetrachloride is not an ideal solvent.

Literature Cited

(1) Walker, J. F. "Formaldehyde", 3rd ed.; Reinhold: New York, 1964.
(2) Lyobomilow, V. I.; Cherkasskaya, E. L. *J. Appl. Chem. USSR (Engl. Transl.)* **1966**, *39*, 683.
(3) Sharan, K. M.; Swarup, J.; Sagu, M. L.; Rawat, D. S. *Chem. Era* **1978**, *14*, 397.
(4) Fischer, K. *Angew. Chem.* **1935**, *48*, 394.
(5) Tanenbaun, M.; Bricker, C. E. *Anal. Chem.* **1951**, *23*, 354.
(6) SMA-4 (Celanese method) given in a guide book on formaldehyde by Celanese Chemical Co., New York.
(7) Bares, Jiri; Cerny, Cestmir; Fried, Vojtech; Pick, Jiri. "Collection of Problems in Physical Chemistry"; Pergamon Press: Elmsford, NY, 1961; p 247.
(8) Berling, A. A.; Volfson, S. A.; Olenik, E. F.; Yenikolopyan, N. S. *Polym. Sci. USSR (Engl. Transl.)* **1970**, *12*, 506.

Simple Method for the Calculation of Heat Capacities of Liquid Mixtures

Amyn S. Teja

School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332

A simple method based on the corresponding state principle is proposed for the calculation of the heat capacities of liquid mixtures. The method requires a knowledge of the heat capacities of two pure liquids as a function of temperature. For the 16 binary liquid mixtures studied in this work, average absolute deviations (AADs) between experimental and calculated heat capacities were found to be 3.03% when only the pure-component heat capacities were used in the calculations and 1.44% when binary data at a single temperature were used. The method is simple to use and can easily be generalized to multicomponent mixtures.

The heat capacity of liquids and liquid mixtures is important in many heat-transfer calculations (appearing, for example, in the Prandtl number and in enthalpy expressions). Although there are a number of heat capacities in common use, the heat

capacity at constant pressure C_p is of greatest interest in heat-transfer work. The heat capacity of the saturated liquid C_{sat} is also of interest, but the difference between C_p and C_{sat} is usually negligible.

There are a number of estimation methods for the heat capacities of pure liquids (1). However, very few specific correlations have been suggested for mixtures. Normally, the use of an arithmetic mole or weight fraction average of the pure-component values is recommended (1) although this neglects any contribution due to the temperature variation of the enthalpy of mixing. Thus

$$C_{pm} = w_1 C_{p1} + w_2 C_{p2} \quad (1)$$

or

$$C_{pm} = x_1 C_{p1} + x_2 C_{p2} \quad (2)$$

Recently, Jamieson and Cartwright (2) assessed the effective-