

A Fortran IV program was written to evaluate Λ_0 from the results in Table I; it was based on assigning an initial value to Λ_0 , estimated from the Λ vs. $[\text{TFA}]^{1/2}$ plot (Figure 2). The iterative process converged rapidly, giving a true value of Λ_0 , provided that the trial of Λ_0 was within a factor of 4 of the true value. Self-consistent values of Λ_0 and K were evaluated from the intercept and slope, respectively, of the plot shown in Figure 3 where the ordinate and abscissa have their usual significance (10). These results are given in Table III together with values of ΔH_3° obtained from the plot in Figure 4 and ΔG_3° and ΔS_3° evaluated by standard relationships.

No other data are available for comparison purposes, with the exception of a specific conductance value for $4 \times 10^{-2} M$ perchloric acid in dichloromethane of $9 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25°C quoted by Gandini and Plesch (5). This compares with our value of $2.8 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$ for TFA in DCE (with similar dielectric constant) at the same concentration and temperature. This parallels the known order of acid strengths of the two acids in water.

LITERATURE CITED

- (1) Carjaval, C., Toller, K. J., Smid, J., Szwarc, M., *J. Amer. Chem. Soc.*, **87**, 5548 (1965).
- (2) Fuoss, R. M., *ibid.*, **57**, 488 (1935).
- (3) Fuoss, R. M., Kraus, C. A., *ibid.*, **55**, 476 (1933).
- (4) Fuoss, R. M., Shedlovsky, T., *ibid.*, **71**, 1496 (1949).
- (5) Gandini, A., Plesch, P. H., *J. Chem. Soc. B*, **1966**, p 7.
- (6) International Critical Tables, 1st ed., III, 28, New York, N.Y., 1928.
- (7) *Ibid.*, VII, 213, New York, N.Y., 1930.
- (8) Kraus, C. A., Fuoss, R. M., *J. Amer. Chem. Soc.*, **55**, 4765 (1933).
- (9) Maryott, A. A., Smith, E. R., "Table of Dielectric Constants of Pure Liquids," Natl. Bur. Stand. Circ. 514, 1951.
- (10) Mead, D. J., Fuoss, R. M., Kraus, C. A., *Trans. Faraday Soc.*, **32**, 594 (1936).

RECEIVED for review September 13, 1971. Accepted December 23, 1971.

Method for Determining Solubility of Slightly Soluble Organic Compounds

WILLIE CHEY and GEORGE V. CALDER¹

Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa 50010

A method for measuring the solubility of slightly soluble organic compounds is described. The procedure involves the quantitative extraction of the solute using nonpolar resins, elution of the sorbed solute, and analysis of the eluent. The accuracy of the method is comparable to other methods and does not suffer their limitations.

Solubility data for slightly soluble organic compounds are sparse in the literature because few general methods exist for obtaining the data. Moreover, those methods which do exist, such as radioactive isotopic labeling, ultraviolet spectrophotometry, and aqueous injection gas chromatography, all have limitations. Tracer techniques require sophisticated expensive equipment. Spectrophotometry possesses the requisite sensitivity for only certain classes of compounds and is often subject to interferences from other compounds which may be present in the solution. Direct injection of aqueous solutions into gas chromatographic columns often produces a large "tail" that masks the minor component being analyzed quantitatively.

This report describes a method for determining the solubility of nonionic organic compounds in water that circumvents many of these limitations of existing methods and uses only standard laboratory methods and equipment. The method involves the quantitative absorption of the dissolved organic compound on a macrorreticular resin bed, followed by elution with an appropriate solvent and quantitative analysis of the eluent. The absorption of the solute on the resin serves the threefold purpose of separating the solute from the aqueous solution, concentrating the solute for increased sensitivity, and transferring the solute to a more convenient solvent for analysis. The method was tested on benzene, toluene, and chlorobenzene, the solubility of which has been measured using other techniques. For these compounds gas chromatography was a convenient analytical tool.

Macrorreticular resins have been used to extract various organic compounds from water (1). Previous work in these

laboratories has shown that a wide range of organic compounds are quantitatively extracted from water even when present at sub ppm concentration levels (5). Aliphatic compounds containing more than four or five carbon atoms and virtually all aromatic compounds are quantitatively absorbed. On the other hand, both inorganic and organic ions, such as Na^+ or Cl^- , pass unhindered through the resin bed. Thus it is possible to extract and analyze nonionic compounds in the presence of ions that might interfere with spectrophotometric methods.

PROCEDURE

A thermostated ($21^\circ \pm 1^\circ\text{C}$) separatory funnel containing about 50 ml of distilled water and about 1 ml of the organic solute (A. R. Grade) was allowed to stand for 10–20 hr with occasional stirring in order to come to equilibrium. A weighed amount of the saturated solution was added dropwise to a 1-cm diam \times 7-cm long column of XAD-2 macrorreticular resin until 20–40 grams of solution had been removed. The tip of the separatory funnel was kept submerged under distilled water covering the resin bed to minimize the possibility of evaporation of the solute during the absorption step. About 30 ml of isopropyl ether was used to elute the sorbed compound from the column. By observing the water–ether interface as it proceeded down the column, it was possible to collect the first 10–20 ml of eluent. Separate experiments verified that the compounds tested were quantitatively retained by the resin and that the elution was complete after about 10 ml of eluent passed through the bed. After the eluent was weighed, about 10 pellets of molecular sieve were added to remove the small

¹ To whom correspondence should be addressed.

Table I. Solubility of Benzene, Toluene, and Chlorobenzene in Water

	Weight in vacuo, grams		Ratio of gas chro- matograph peak areas	Concn of std soln, g/g soln	Solubility (21° ± 1°C) g/100 g H ₂ O	Mean value	Av dev measure- ments	% Dev from mean lit. value	Lit. value, g/ 100 g H ₂ O	Ref.
	H ₂ O soln	Eluent								
Benzene	24.7267	11.1539	0.7936	0.004968	0.178			2.3	0.171 ± 0.002	(3)
	37.2681	11.6291	0.8774	0.005548	0.152	0.174	0.011	12	0.179	(4)
	37.3462	9.4237	1.3067	0.005548	0.183			5.2	0.174	(6)
	39.9882	10.0274	1.3197	0.005548	0.184			3.7	0.174	(2)
Toluene	30.4742	9.0561	0.2401	0.005515	0.0394			7		
	28.2919	9.1872	0.3388	0.005515	0.0607	0.0479	0.0086	32	0.0627	(4)
	19.7750	4.5221	0.3810	0.004968	0.0435			25	0.055	(7)
Chlorobenzene	35.4719	10.1696	0.3426	0.005556	0.0546	0.0534	0.0011	11	0.050	(8)
	29.9234	11.2880	0.2492	0.005556	0.0523			4		

amount of water dissolved in the isopropyl ether. Separate experiments verified that the solute concentration was unaffected by the addition of the molecular sieve. A 1.5- μ l. sample of the ether solution was injected into a Carle gas chromatograph Model 8004 fitted with a 5 ft \times 1/8 in. o.d. stainless steel column packed with 80-100 mesh Chromosorb which supported a 15% by weight liquid phase of Carbowax 20M. A flow rate of 15 cc He/min at 25°C was used, and the effluents were detected by a dual thermistor. The sample inlet, column, and detector were maintained at 100°C. Immediately before or after each sample injection the chromatograph was calibrated using a standard solution of the compound in isopropyl ether. The areas of the peaks were measured planimetrically. The recorder parameters were adjusted so as to maintain a peak height to peak width ratio between 10:1 and 5:1 to minimize errors in the planimetry.

RESULTS AND DISCUSSION

The solubility of the test compounds—benzene, toluene, and chlorobenzene—presented in Table I are generally in good agreement with values obtained from other methods. Because the purpose of this work was only to demonstrate the feasibility of the method, certain experimental variables were not so rigidly controlled as would be desired for accurate quantitative data. For example, the water should be deaerated and care-

fully thermostated, equilibrium of the solute should be checked by successive determinations over an extended period of time, and light scattering experiments should be carried out on the solution to ensure that the solute is not suspended in the solution rather than relying on visual examination. The data suggest that results of the order of 5-10% accuracy are possible even without these precautions, and that results of accuracy comparable to more sophisticated methods are attainable.

LITERATURE CITED

- (1) "Amberlite XAD Macroreticular Absorbants," Rohm and Haas Co., Philadelphia, Pa., 1970.
- (2) Andrews, L. J., Keefer, R. M., *J. Amer. Chem. Soc.*, **71**, 3645 (1949).
- (3) Arnold, D. S., Plank, C. A., Erickson, E. E., Pike, F. P., *J. Chem. Eng. Data*, **3**, 253 (1958).
- (4) Bohon, R. L., Claussen, W. F., *J. Amer. Chem. Soc.*, **73**, 1571 (1951).
- (5) Burnham, A. K., Calder, G. V., Fritz, J. S., Junk, G. A., Svec, H. J., Willis, R., *Anal. Chem.*, **44**, 139 (1972).
- (6) Dreisbach, R. R., *Advan. Chem. Ser.*, **15**, 11 (1955).
- (7) Dreisbach, R. R., *ibid.*, p 12.
- (8) Dreisbach, R. R., *ibid.*, p 134.

RECEIVED for review September 15, 1971. Accepted December 16, 1971. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

Electrical Conductance of Binary Nitrate Mixtures

HARISH C. GAUR¹ and SURENDER K. JAIN

Department of Chemistry, University of Delhi, Delhi-7, India

The electrical conductance of molten NaNO₃-Sr(NO₃)₂, KNO₃-Sr(NO₃)₂, NaNO₃-Pb(NO₃)₂, KNO₃-Pb(NO₃)₂, AgNO₃-Pb(NO₃)₂, and TlNO₃-Pb(NO₃)₂ mixtures has been measured as a function of temperature and the divalent ion content in the mixture.

The electrical conductance of molten alkali metal nitrates and their binary/ternary mixtures has been reported by several workers (2, 3, 11-14). There are relatively fewer such studies for the mixtures of monovalent and divalent/trivalent metal nitrates. In continuation of our previous studies of such mixtures (4-7), specific conductance data for the systems (Na,K)-NO₃-(Sr, Pb)(NO₃)₂, (Ag, Tl)NO₃-Pb(NO₃)₂ at various com-

positions and over a wide temperature range are presented in this paper.

EXPERIMENTAL

LR(BDH)-grade thallium and strontium nitrates were recrystallized from demineralized water. All other reagents were of AnalaR (BDH) grade; these were desiccated in the following

¹ To whom correspondence should be addressed.