Akgerman (*1*) based on significant liquid structure and absolute rate theory works better than all the other expressions. The Wilke-Chang Equation, although as accurate for many systems, is inaccurate when the solute is a small molecule like hydrogen or helium or when solvent is a viscous liquid. The Stokes-Einstein and the Eyring equations are inaccurate, perhaps due to the questionable assumptions in their derivations leading to the final expressions. The Othmer and Thakar expression, on the other hand, cannot predict the temperature dependency of diffusion coefficients and is inaccurate for nonaqueous solvents.

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RECEIVED for review August 3, 1971. Accepted January 4, 1972. A complete computer readout of Table I will appear following these pages in the microfilm edition of this volume of the Journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Refer to author, title of article, volume, and page number. Remit by check or money order $4.00 for photocopy or $2.00 for microfiche.

Solubility of Hydrohalogens in Normal C_5–C_{16} Alcohols

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Data on the solubility of HBr and HCl in *n*-C_5–C_{16} alcohols are presented. Heat of solution of HBr into the above alcohols in the temperature range of 100–60°C is about 10,500 cal/mol.

Higher molecular weight alkyl halides, such as lauryl bromide and cetyl chloride, are used in making detergents and germicides (*1, 4, 9, 10*). One method of making these alkyl halides is to react hydrogen bromide and hydrogen chloride gases with the corresponding alcohols at temperatures on the order of 120–60°C. The solubility of HBr and HCl in these alcohols must be known in order to interpret the kinetic data of the absorption of HBr and HCl. Fernandes and Sharma (*2*) have reported the solubility of HCl in *n*-C_{12}–*n*-C_{18} alcohols in the temperature range of 30–200°C. Ionin et al. (*8*) and Gerrard et al. (*6*) have reported solubilities of HCl in *n*-C_1–*n*-C_{10} alcohols at temperatures up to 60°C and of HBr in *n*-octanol and so forth at only one temperature of 15°C. There is no other information available for the solubility of HBr in alcohols higher than *n*-C_8 and also at higher temperatures. In this work, data on the solubility of HBr in *n*-C_5–*n*-C_{18} alcohols in the temperature range of 15–160°C are presented.

MATERIALS

HBr gas supplied by Matheson Co. was of 99.8% purity (99% min purity). Alcohols supplied by K and K Labora-

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Table I. Solubility of HBr in *n*-Alcohols

Expressed as moles of HBr per mole of n-ROH at a partial pressure of 760 mm of Hg

	Temperature, °C									
Alcohol	15	25	30	40	60	80	100	120	140	160
Amyl, C_5	1.062[a]	0.953[a]	...	0.71[a]	0.501[a]	0.338[a]	...	...	...	...
Hexyl, C_6	1.078	...	...	0.704[a]	0.4655[a]	0.34[a]	...	...	...	...
Heptyl, C_7	1.04	...	0.964	0.72	0.438[a]	...	...	...	...	...
Octyl, C_8	1.08	...	0.91	0.772	0.474[a]	...	...	...	...	...
Nonyl, C_9	1.05	...	...	0.797	0.481	0.242[a]	...	...	...	...
Decyl, C_{10}	1.06	0.94	0.89	0.771	0.54	0.39[a]	0.303[a]	0.124[a]	0.063[a]	...
Dodecyl, C_{12}	[b]	0.89	...	0.79	0.54	0.391[a]	0.312	0.1321[a]	0.0523[a]	0.031[a]
Tetradecyl, C_{14}	[b]	[b]	[b]	[b]	0.43	0.306	...	...	0.0571[a]	0.029[a]
Cetyl, C_{16}	[b]	[b]	[b]	[b]	0.461	0.236	...	...	0.0512[a]	...

[a] Vapor pressure correction applied (acid-base titration method used here). [b] The materials are solids at the temperature indicated.

tories were of reagent grade (99% min purity). Both the gas and the alcohols were used as such.

EXPERIMENTAL

Two methods were used for determining the solubility of HBr in alcohols; the weight increase method and the acid-base titration method. The weight increase method was used only at such temperatures when the estimated vapor pressure of the alcohols was below 1 mm of Hg. The maximum error that may occur due to the carry-over of alcohol in a period of 2 hr was found to be less than 1% by weight. In this method, about 15–20 grams of alcohols were taken in a previously cleaned, dried, and weighed saturator. The saturator and the contents were immersed into a previously adjusted thermostat until the temperature of alcohol reached a steady value. Hydrogen bromide gas was then passed through the alcohol for about 1 hr. The amount of HBr gas dissolved in the alcohol was determined by the increase in weight of the saturator. This was repeated until two consecutive readings were the same.

At temperatures when the alcohols exerted vapor pressure above 1 mm of Hg, the acid-base titration method was used. In this method, about 1–2 ml of a sample of saturated alcohol were taken in a previously cleaned, dried, and weighed sample tube; weighed once again and then transferred to a conical flask containing a known amount of chilled aqueous solution of sodium hydroxide. HBr was completely extracted into the aqueous phase by heating the whole mass just above the melting point of the alcohol. The extracted HBr reacted with NaOH and the remaining NaOH was determined by titrating it with an acid. At lower temperatures both methods were used initially, and the values of solubilities obtained by both the methods agreed within 1% by weight.

RESULTS AND DISCUSSION

Solubility of HBr in *n*-octanol at 15°C was determined by both the methods to check their accuracy: 1.08 moles of HBr per mole of *n*-octanol by both the methods, which is within 3% of the value reported by Gerrard et al. (*6*) (1.05 moles of HBr per mole of *n*-octanol). Solubility of HBr in *n*-C_5–*n*-C_{16} is reported in Table I.

This work shows that in the range of temperature from 15–160°C, the solubility of HBr expressed as mole of HBr per mole of ROH is very nearly the same in the alcohols ranging from *n*-C_5–*n*-C_{16}. A similar type of behavior was reported by Gerrard et al. (*5–7*) in the case of the solubility of HCl in *n*-C_1–*n*-C_{10} alcohols up to a temperature of 60°C and Fernandes and Sharma (*2*) in *n*-C_{12}–*n*-C_{18} alcohols up to a temperature of 200°C. Figure 1 is the plot of log solubility of HBr in *n*-C_{12} alcohol (expressed as mole fraction of HBr) vs. $1/T$ (T in K) in the temperature range from 15–160°C. It shows that the plot is a straight line in the temperature range of 100–60°C. Below 100°C, this plot is not a straight line indicating that the solution is not ideal. However, Figure 2 is the plot of solubility of HBr in *n*-C_{12} alcohol, expressed as mole of HBr per mole of ROH vs. $1/T$ (as T in K) plotted by Gerrard et al. (*5–7*) is a straight line up to 100°C. Hence, it is likely that the temperature at which the "loose compound" decomposes almost completely is about 100°C.

Solubility of HCl in *n*-C_6, *n*-C_8, and *n*-C_{10} alcohols in the temperature range of 80–140°C is reported in Table II (*3*).

Table II. Solubility of HCl in *n*-Alcohols

At a partial pressure of HCl of 760 mm Hg[a] (*9*)

	Temperature, °C						
Alcohol	30	40	60	80	100	120	140
Hexyl, C_6	...	...	...	0.434	0.32	0.236	...
Octyl, C_8	0.792[b]	0.716[b]	...	0.389	0.26	0.129	0.0785
Decyl, C_{10}	0.800[b]	0.712[b]	0.567[b]	0.385	0.232	0.109	0.0655

[a] Vapor pressure correction applied. [b] Interpolated from values in ref. 7.

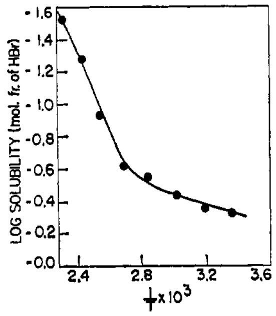

Figure 1. Plot of log solubility (mole fraction of HBr) vs. 1/T

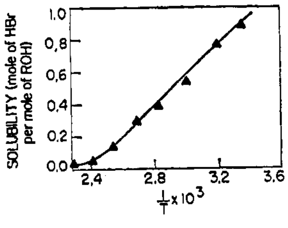

Figure 2. Plot of solubility (mole of HBr per mole of ROH) vs. 1/T

The acid-base titration method previously described ("Experimental") was used for determining the solubility of HCl reported in Table II. The solubility of HCl in *n*-butanol at 45°C was obtained to check the accuracy of the method: 0.66 mole of HCl per mole of *n*-butanol, which is the same as the value reported by Gerrard (*7*). The solubility of HCl expressed as mole of HCl per mole of ROH is very nearly the same in the temperature range of 80–140°C also. Ionin et al. (*8*) and Gerrard et al. (*5–7*) have shown similar behavior only up to a temperature of 60°C.

ACKNOWLEDGMENT

The author wishes to thank M. M. Sharma for encouragement and George Burnet, Jr., for arranging the funds.

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RECEIVED for review August 20, 1970. Resubmitted September 20, 1971. Accepted April 13, 1972. Work supported by the Engineering Research Institute, Iowa State University.

ORGANIC SECTION

Ternary Liquid Equilibrium Systems Ethanol–Water–Methyl Isobutyl Carbinol and Acetic Acid–Water–Ethyl Butyrate

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Phase equilibrium data for the ternary liquid-liquid systems ethanol–water–methyl isobutyl carbinol and acetic acid–water–ethyl butyrate were determined at three temperatures adopting the method of Othmer, White, and Trugger and a new method which is a simple modification of the same. There is fair agreement between the data obtained by both methods. The tie-line data were correlated by the methods of Hand and Othmer and Tobias. The effect of temperature on distribution is slight. In the system ethanol–water–methyl isobutyl carbinol, the solute is in greater weight fraction in the solvent phase, and in the system acetic acid–water–ethyl butyrate, the solute is present in greater weight fraction in the aqueous phase.

The aim of the present investigation is to determine the phase-equilibrium data for the systems ethanol–water–methyl isobutyl carbinol and acetic acid–water–ethyl butyrate at three different temperatures and atmospheric pressure using a method which is a simple modification of the method of Othmer et al. (*3*) for determining the weight fraction of the components in each of the phases in heterogeneous ternary liquid-liquid systems. The proposed method, despite its limitations, is useful for such systems where the determination of the tie-line data is limited by the accuracy of the analytical methods. The phase-equilibrium data at 28°C for the system acetic acid–water–ethyl butyrate were reported earlier by Ramana Rao and Dakshinamurty (*4*).

MATERIALS

Absolute alcohol was used. Methyl isobutyl carbinol from the British Drug House was fractionated; the fraction boiling between 131.5° and 132°C was collected and used (density at 30° = 0.8003 g/cc and refractive index at 30°C = 1.4090 for sodium D line). Acetic acid from the British Drug House, analar grade of 99.8% purity, having a density at 30°C of 1.0365 and a refractive index at 30°C of 1.3680 was used. Ethyl butyrate (Naarden Co., density at 30°C = 0.8685 and refractive index at 30°C = 1.3880) with negligible free acidity was used.

PROCEDURE

Weighed mixtures having a constant ratio of x_c/x_w, x_w/x_s, or x_s/x_c and increasing amounts of the third component were placed in a borosilicate glass test tube (20 cc) with a ground glass joint, and fitted with a thermometer. The test tube was slowly heated or cooled in a water bath and the temperature, corresponding to the appearance or disappearance of turbidity, was noted. The end points were reproducible to ±0.5°C either on heating or cooling. Thus, the phase-equilibrium

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