(10) Spedding, F. H., Baker, J. L., Walters, J. P., *J. Chem. Eng. Data,* **20,** 189 (1975).
(11) Spedding, F. H., Csejka, D. A., DeKock, C. W., *J. Phys. Chem.,* **70,** 2423 (1966).
(12) Spedding, F. H., Cullen, P. F., Habenschuss, A., *J. Phys. Chem.,* **78,** 1106 (1974).
(13) Spedding, F. H., Naumann, A. W., Eberts, R. E., *J. Am. Chem. Soc.,* **81,** 23 (1959).
(14) Spedding, F. H., Pikal, M. J., Ayers, B. O., *J. Phys. Chem* , **70,** 2440 (1966).
(15) Spedding, F. H., Saeger, V. W., Gray, K. A., Boneau, P. K., Brown, M. A., DeKock, C. W., Baker, J. L., Shiers, L. E., Weber, H. O., Habenschuss, A., *J. Chem. Eng. Data,* **20,** 72 (1975).
(16) Spedding, F. H., Shiers, L. E., Brown, M. A., Baker, J. L., Gutierrez, L., McDowell, L. S., Habenschuss, A., *J. Phys. Chem.,* **79,** 1087 (1975).
(17) Spedding, F. H., Shiers, L. E., Brown, M. A., Derer, J. L., Swanson, D. L., Habenschuss, A., *J. Chem. Eng. Data,* **20,** 81 (1975).
(18) Spedding, F. H., Shiers, L. E., Rard, J. A., *J Chem. Eng. Data,* **20,** 88 (1975).
(19) Vanderzee, C. E., Nutter, J. D., *J. Chem. Eng. Data,* **19,** 268 (1974).
(20) Wagman, D. D., Evans, W. H., Parker, V. B., Halow, I., Bailey, S. M., Schumm, R. H., *Natl. Bur. Stand. (U.S.), Tech. Note,* **No. 270-(1-6)** (1968–1971).
(21) Wallace, W. E., Robinson, A. L., *J. Am. Chem. Soc.,* **63,** 958 (1941).
(22) Young, T. F., Groenier, W. L., *J. Am. Chem. Soc.,* **58,** 187 (1936).
(23) Young, T. F., Seligman, P., *J. Am. Chem. Soc.,* **60,** 2379 (1938).
(24) Young, T. F., Vogel, O. G., *J. Am. Chem. Soc.,* **54,** 3030 (1932).
(25) Zinov'ev, A. A., Shchirova, N. A., *Russ. J. Inorg. Chem.,* **5,** 626 (1960).

Received for review February 24, 1976. Accepted October 8, 1976. This report was prepared for the U.S. Energy Research and Development Administration under Contract No. W-7405-eng-82, and is based in part, on the Ph.D. dissertations of M. A. Mohs (1970) and J. L. Derer (1974) submitted to the Graduate Faculty of Iowa State University, Ames, Iowa 50010.

Vapor–Liquid Equilibrium Constants of Alkylbenzenes in *n*-Alkane Solvents at Infinite Dilution by Gas–Liquid Chromatography

Toshiaki Sugiyama,*[†] Tsugio Takeuchi, and Yoshihito Suzuki
Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Nagoya, Japan

Vapor–liquid equilibrium constants at infinite dilution of benzene and alkylbenzenes in *n*-octacosane, *n*-dotriacontane, and *n*-hexatriacontane solvents were measured by gas–liquid chromatography at five temperatures, 78.0, 84.0, 90.0, 96.0, and 102.0 °C. The thermodynamic properties of solution of alkylbenzenes from the gas phase to *n*-alkane solvent were also determined from the data of vapor–liquid equilibrium constants. The partial molar enthalpy of solution is related with the structure of alkylbenzenes through an equation by a set of values of structural parameters.

The properties of molecules in liquid phases have been greatly studied by experimental methods of static and dynamic techniques. Theoretical approaches of the behavior of molecules in pure liquids and liquid mixtures are mainly limited to ideal or simple liquid systems. Study for theoretical research demands therefore determining the thermodynamic properties of liquid in simple systems. In liquids consisting of pure substance, molecules frequently have association by hydrogen bonding or other strong intermolecular interaction. The molecular association distorts the liquid phase from the ideal to nonideal liquid system, e.g., polyassociation of alcohols. In solutions at infinite dilution, solute molecules no longer associate with each other, but associate with surrounding solvent molecules since the solute molecule is enveloped by solvent molecules only. Thermodynamic properties of solute molecules are highly dependent on the nature of solvent molecules. The variation of the thermodynamic properties with solvents will give us the characteristics of many interacting abilities of solute molecules, such as dispersion, induced dipole, dipole–dipole interaction, Coulomb force, charge transfer interaction, coordinate bond, and hydrogen bonding energies. Solution at infinite dilution is an ideal state for solute molecules. The properties of the solution are easily combined with current theories of solutions of molecules. Gas–liquid chromatography (GLC) provides the properties at infinite dilution on the basis of GLC conditions. Recently, GLC is a rapid and reliable method for determinination of accurate thermodynamic properties (*1, 2, 4–12, 15–21*).

In this paper, GLC was used here to study alkylbenzenes in three high-molecular-weight normal alkane solvents. Vapor–liquid equilibrium constants at infinite dilution are obtained at five temperatures. Heat of solution from the gas phase to *n*-alkane solvent is also determined and can be given by a relation with structure of the solute molecule by a consistent set of parameters.

Experimental Section

The gas chromatograph used was an Hitachi K53 equipped with a thermal conductivity detector. Column temperatures for measurement of retention volumes are 78.0, 84.0, 90.0, 96.0, and 102.0 °C. The column temperatures were maintained constant within 0.1 °C. Hydrogen was used as a carrier gas. The carrier gas flow rate was measured at room temperature with a soap-film flowmeter placed at the detector outlet. Inlet and outlet pressure of carrier gas was determined to 0.1 mmHg by mercury manometers.

Three stationary liquid phases were used: *n*-octacosane ($n\text{-}C_{28}H_{58}$), *n*-dotriacontane ($n\text{-}C_{32}H_{66}$), and *n*-hexatriacontane ($n\text{-}C_{36}H_{74}$). These phases were obtained from the Tokyo Chemical Industry Co., Ltd., Tokyo, Japan. $n\text{-}C_{32}H_{66}$ was purified three times by recrystallization from ethanol, while $n\text{-}C_{28}H_{58}$ and $n\text{-}C_{36}H_{74}$ were purified once similarly.

Benzene, toluene, ethylbenzene, *p*-, *m*-, and *o*-xylenes, cumene, and 1,3,5-, 1,2,4-, and 1,2,3-trimethylbenzenes were chosen for this study of alkylbenzenes and used without further purification.

The liquid for stationary phase was coated on to solid support material in the usual manner. The solid support used was Celite 545, 80–100 mesh, hexamethyldisilazane (HMDS) treated. The amount of each liquid phase on the support material was changed from 10 to 15 wt %. The coated support material was packed into 1 m × 3 mm i.d. stainless steel tubing. For reference, stationary-liquid-uncoated support material was also packed into different tubing. Each column was conditioned at 110 °C for about 24 h with a gentle flow of a carrier gas. The smallest detectable sample sizes were used at all times so as to ensure operation in the Henry's law region of solute con-

---

[†] Address correspondence to this author at the Department of Industrial Chemistry, Suzuka College of Technology, Shiroko-cho, Suzuka, Mie, Japan.

Table I. Comparison of Experimental Specific Retention Volumes, V_g/cm^3 g^{-1} [a]

Solute	This work	Ref 19
Benzene	76.75	72.57
Toluene	187.0	183.5
p-Xylene	441.7	442.3
m-Xylene	446.6	446.4
o-Xylene	526.6	522.0
Ethylbenzene	384.7	379.7
Cumene	610.5	604.1

[a] Column temperature, 84.0 °C; stationary phase, *n*-$C_{36}H_{74}$.

centrations. Samples were injected together with a small detectable amount of air. Retention times of samples were corrected by an air peak. The exact weight of stationary liquid was determined by Soxhlet extraction with *n*-hexane after all experiments.

Results and Discussion

Specific Retention Volumes. Specific retention volume, V_g, is calculated from the corrected peak retention time and the column operating conditions. For each stationary liquid, samples were run on several columns with different liquid weight percentages. Flow rate of the carrier gas was changed from 4 to 20 mL min^{-1} for each sample and each column. Both influences on the specific retention volume were found to vary by less than 1%. In the case of the column where stationary liquid was not coated on solid support material, the separation of gas chromatographic peaks between air and *n*-heptane cannot be found under the experimental conditions. The adsorption of solute on the support material is almost negligible. The treatment of HMDS gives also no effect for vapor-liquid equilibrium.

Average values of V_g are calculated from data under various experimental conditions. Specific retention volumes obtained in this work are compared with published values in Table I.

Vapor-Liquid Equilibrium Constants. The vapor-liquid equilibrium constant, K_p, of solute in solution is generally given as follows:

$$K_p = \frac{p_2}{N_2/(N_1 + N_2)} \tag{1}$$

where p_2 is the vapor pressure of solute in the vapor phase in equilibrium with a liquid mixture consisting of N_1 molecules of solvent and N_2 molecules of solute. Accurately speaking, p_2 in eq 1 must be expressed in the term of *fugacity*, f_2, of solute. The relation between *apparent partial pressure* p_2 and *fugacity* f_2 can be shown as follows (*3*):

$$\ln f_2 = \ln p_2 + \frac{p}{RT}(2B_{23} - B_{33} - v_2^0) \tag{2}$$

where p is the (mean) total pressure of the gas phase, B_{23} the mixed second virial coefficient of solute vapor and carrier gas, B_{33} the second virial coefficient of carrier gas, and v_2^0 the molar volume of solute. R is the gas constant and T the absolute temperature.

According to the several GLC theories, specific retention volume V_g is related to partition coefficient K_c by

$$V_R = K_c V_1 \tag{3}$$

where V_R is the actual specific retention volume which is the *real* volume of gas passing through the GLC column and related with the currently used specific retention volume V_g by

$$V_R = \frac{T}{273.2} V_g \tag{4}$$

K_c is the ratio of the number of solute molecules in unit volume of liquid phase to the number of solute molecules in unit volume of gas phase. T is absolute column temperature in K. V_1 is the

Table II. Vapor-Liquid Equilibrium Constants at Infinite Dilution, K_p^∞/atm

Solvent	Solute	78.0 °C	84.0 °C	90.0 °C	96.0 °C	102.0 °C
n-$C_{28}H_{58}$	Benzene	0.569	0.677	0.802	0.955	1.117
	Toluene	0.225	0.278	0.341	0.411	0.492
	Ethylbenzene	0.1062	0.1353	0.1684	0.207	0.252
	p-Xylene	0.0923	0.1167	0.1471	0.1807	0.222
	m-Xylene	0.0914	0.1155	0.1459	0.1782	0.222
	o-Xylene	0.0777	0.0989	0.1247	0.1533	0.1906
	Cumene	0.0655	0.0843	0.1067	0.1326	0.1644
	1,3,5-TMB	0.0372	0.0488	0.0629	0.0796	0.1015
	1,2,4-TMB	0.0319	0.0423	0.0545	0.0693	0.0870
	1,2,3-TMB	0.0261	0.0348	0.0440	0.0572	0.0721
n-$C_{32}H_{66}$	Benzene	0.520	0.618	0.730	0.856	0.998
	Toluene	0.208	0.253	0.309	0.368	0.445
	Ethylbenzene	0.0982	0.1229	0.1527	0.1858	0.230
	p-Xylene	0.0845	0.1068	0.1332	0.1638	0.203
	m-Xylene	0.0837	0.1058	0.1313	0.1620	0.202
	o-Xylene	0.0708	0.0899	0.1125	0.1386	0.1728
	Cumene	0.0607	0.0770	0.0972	0.1199	0.1505
	1,3,5-TMB	0.0373	0.0443	0.0571	0.0720	0.0922
	1,2,4-TMB	0.0293	0.0381	0.0494	0.0625	0.0803
	1,2,3-TMB	0.0240	0.0312	0.0405	0.0514	0.0663
n-$C_{36}H_{74}$	Benzene	0.484	0.576	0.686	0.786	0.898
	Toluene	0.1906	0.237	0.281	0.342	0.403
	Ethylbenzene	0.0906	0.1149	0.1397	0.1744	0.210
	p-Xylene	0.0789	0.1001	0.1226	0.1531	0.1854
	m-Xylene	0.0782	0.0990	0.1217	0.1517	0.1846
	o-Xylene	0.0656	0.0840	0.1038	0.1299	0.1576
	Cumene	0.0563	0.0724	0.0895	0.1137	0.1382
	1,3,5-TMB	0.0314	0.0417	0.0529	0.0690	0.0857
	1,2,4-TMB	0.0267	0.0356	0.0450	0.0590	0.0733
	1,2,3-TMB	0.0218	0.0292	0.0370	0.0487	0.0607

specific volume of stationary liquid (solvent). The relationship between vapor–liquid equilibrium constant K_p^∞ at infinite dilution and partition coefficient K_c is given by

$$K_p^\infty = \frac{RT}{M_r V_1} \frac{1}{K_c} \exp\left[\frac{p}{RT}(2B_{23} - B_{33} - v_2^0)\right] \tag{5}$$

where M_r is the molecular weight of stationary liquid. Combination of eq 3 and 5 gives the following equation

$$K_p^\infty = \frac{RT}{M_r V_R} \exp\left[\frac{p}{RT}(2B_{23} - B_{33} - v_2^0)\right] \tag{5'}$$

The appearance of the parameters B_{23} and B_{33} is due to the existence of solute vapor–carrier gas and carrier gas–carrier gas interactions in the gas phase, respectively. If hydrogen is used as a carrier gas, the interactions are very small (*3, 4*). Both magnitudes of second virial coefficients are less than 40 cm^3 for most hydrocarbons. Neglecting the B values, we have relative error of 0.3% in the exponent term. The vapor–liquid equilibrium constant at infinite dilution can be determined by GLC through eq 5′. The results are given in Table II.

Thermodynamics of Solution. At equilibrium, the standard free energy G_2° of solute in the vapor phase and the standard partial molar free energy $\bar{G}_2^\circ$ of the solute in the solution are related by

$$G_2^\circ + RT \ln f_2 = \bar{G}_2^\circ + RT \ln x_2\gamma_2 \tag{6}$$

where f_2 is the *fugacity* of the solute in the vapor phase, x_2 and γ_2 are the molar fraction and the activity coefficient of the solute in the solution, respectively. The partial molar free energy of solution, $\Delta\bar{G}_{soln}$, of the solute from the gas-phase to solution is given by the following equation:

$$\Delta\bar{G}_{soln} = \bar{G}_2^\circ - G_2^\circ = RT \ln f_2 - RT \ln x_2\gamma_2 \tag{7}$$

Standard states are chosen as follows: for the vapor phase, *fugacity* of vapor is 1 atm; for the solution, the solute molecules have molecular interaction characteristics at infinite dilution of solute. This standard state in solution represents that $\gamma_2 \rightarrow 1$ as $x_2 \rightarrow 0$ (*12, 13*). Under the GLC condition, x_2 is always near 0. Hence, activity coefficient of solute γ_2 is 1 under this definition of standard state. The partial molar free energy of solution at infinite dilution $\Delta\bar{G}^\infty{}_{soln}$ is related with the vapor–liquid equilibrium constant at infinite dilution K_p^∞.

$$\Delta\bar{G}^\infty{}_{soln} = RT \ln K_p^\infty \tag{8}$$

The value of $\Delta\bar{G}^\infty{}_{soln}$ was calculated from each experimental result. From the temperature dependence of the partial molar free energy of solution, partial molar enthalpy of solution at infinite dilution, $\Delta\bar{H}^\infty{}_{soln}$, can be determined (*14*).

$$\Delta\bar{H}^\infty{}_{soln} = \left[\frac{\partial(\Delta\bar{G}^\infty{}_{soln}/T)}{\partial(1/T)}\right]_p \tag{9}$$

The values of $\Delta\bar{H}^\infty{}_{soln}$ are given in Table III.

Provided that interactions of molecules, such as dispersion, induced dipole, dipole–dipole, charge transfer, and hydrogen bonding interactions, totally affect the cohesion of molecules in liquid phase, the partial energy of cohesion by a segment of the solute molecule is provided by the addition of the interactions between the segment of solute molecule and surrounding solvent molecules. The cohesive energy over the solute molecule is given by the sum of the partial energies of segments in the solute molecule. The cohesive energy is given by the enthalpy of solution. In the case of alkylbenzenes studied, the following segments are considered: benzene ring and methyl group. Ethyl and isopropyl groups will be omitted in the following consideration since the number of studied benzene derivatives having these groups is respectively unity. Roughly speaking, the cohesive energy of benzenes in solution is given by the sum of the energy of cohesion of benzene ring and methyl groups. The energy of cohesion of benzene ring and methyl groups in a solute molecule is denoted by ΔH_{Ph} and ΔH_{CH_3}, respectively. The segmental cohesive energies ΔH_{Ph} and ΔH_{CH_3} correspond to the interaction energies between benzene ring and methyl groups and the surrounding solvent molecules in solution, respectively. The cohesive energy of an alkylbenzene, therefore, can be given by

$$\Delta\bar{H}^\infty{}_{soln} = \Delta H_{Ph} + m\Delta H_{CH_3} \tag{10}$$

where m is the number of methyl groups in the alkylbenzene molecule. Actually, alkylbenzenes having the same number of methyl groups in a molecule have different cohesive energies. It must be considered that the position of a substituent affects the cohesive energy of solute molecules. The energy of cohesion of a methyl substituent is varied by other substituents by Δh. The value of the effect of the para, meta, and ortho position of methyl substituents upon the energy of cohesion is represented by $\Delta h_{p\text{-}CH_3}$, $\Delta h_{m\text{-}CH_3}$, and $\Delta h_{o\text{-}CH_3}$, respectively. The following equation gives the partial molar enthalpy of solution from the gas phase to infinite dilute solution.

$$\Delta\bar{H}^\infty{}_{soln} = \Delta H_{Ph} + m\Delta H_{CH_3} + \sum_{i=1}^{m} (n_{p\text{-}CH_3}\Delta h_{p\text{-}CH_3} + n_{m\text{-}CH_3}\Delta h_{m\text{-}CH_3} + n_{o\text{-}CH_3}\Delta h_{o\text{-}CH_3}) \tag{10'}$$

where m is the number of methyl substituents. $n_{p\text{-}CH_3}$ is the number of methyl groups on para position to the position of the ith methyl substituent. The others are as same as $n_{p\text{-}CH_3}$. For

Table III. Partial Molar Enthalpies of Solution at Infinite Dilution, $-\Delta\bar{H}^\infty{}_{soln}$/kJ mol^{-1}

Solute	Solvent n-$C_{28}H_{58}$	 n-$C_{32}H_{66}$	 n-$C_{36}H_{74}$
Benzene	30.914 ± 0.230[a]	29.761 ± 0.087	28.289 ± 0.824
	30.963 (0.049)[b]	29.744 (−0.017)	28.428 (0.139)
Toluene	35.663 ± 0.310	34.652 ± 0.311	34.088 ± 0.613
	35.518 (−0.145)	34.704 (0.052)	33.672 (−0.416)
Ethylbenzene	39.303 ± 0.476	38.645 ± 0.336	38.401 ± 0.568
	—	—	—
p-Xylene	39.995 ± 0.380	39.835 ± 0.223	38.962 ± 0.472
	40.081 (0.086)	39.890 (0.055)	39.080 (0.118)
m-Xylene	40.293 ± 0.409	39.933 ± 0.334	39.172 ± 03357
	40.392 (0.099)	39.811 (−0.122)	39.465 (0.293)
o-Xylene	40.794 ± 0.352	40.391 ± 0.281	39.971 ± 0.527
	40.753 (−0.041)	40.405 (0.014)	39.976 (0.005)
Cumene	41.881 ± 0.386	41.269 ± 0.336	41.063 ± 0.644
	—	—	—
1,3,5-TMB	45.609 ± 0.336	45.012 ± 0.321	45.883 ± 0.720
	45.584 (−0.025)	45.064 (0.052)	45.806 (−0.077)
1,2,4-TMB	45.720 ± 0.603	45.793 ± 0.319	46.051 ± 0.826
	45.634 (−0.086)	45.738 (−0.055)	45.933 (−0.118)
1,2,3-TMB	46.242 ± 0.608	46.233 ± 0.320	46.771 ± 0.858
	46.306 (0.064)	46.253 (0.020)	46.828 (0.057)

[a] Experimental value with standard deviation. [b] Calculated value with deviation in parentheses.

Table IV. Parameters for Prediction of Enthalpy of Solution through Equation 10′ (in kJ mol^{-1})

Parameter	Solvent n-$C_{28}H_{58}$	 n-$C_{32}H_{66}$	 n-$C_{36}H_{74}$
$-\Delta H_{Ph}$	30.963 ± 0.130	29.744 ± 0.092	28.428 ± 0.312
$-\Delta H_{CH_3}$	4.556 ± 0.123	4.960 ± 0.087	5.244 ± 0.295
$-\Delta h_{p\text{-}CH_3}$	0.004 ± 0.079	0.113 ± 0.056	0.082 ± 0.190
$-\Delta h_{m\text{-}CH_3}$	0.159 ± 0.051	0.073 ± 0.036	0.274 ± 0.123
$-\Delta h_{o\text{-}CH_3}$	0.340 ± 0.057	0.371 ± 0.040	0.530 ± 0.137

example, 1,2,4-trimethylbenzene is given by

$$\Delta \bar{H}^{\infty}{}_{\text{soln}} = \Delta H_{\text{Ph}} + 3\Delta H_{\text{CH}_3} + (\Delta h_{p\text{-CH}_3} + \Delta h_{o\text{-CH}_3}) + (\Delta h_{m\text{-CH}_3} + \Delta h_{o\text{-CH}_3}) + (\Delta h_{p\text{-CH}_3} + \Delta h_{m\text{-CH}_3})$$

By means of the method of least squares, these five parameters ΔH_{Ph}, ΔH_{CH_3}, $\Delta h_{p\text{-CH}_3}$, $\Delta h_{m\text{-CH}_3}$, and $\Delta h_{o\text{-CH}_3}$ are determined with little standard deviations from the data of the partial molar enthalpy of solution. The parameters are efficient in the systems of long chain n-alkane solvents at infinite dilution. The values of parameters are given in Table IV. The predicted value of the enthalpy of solution can be determined through eq 10′. The calculated values are given in Table III. Equation 10′ provides very good agreement between experimental and calculated enthalpy of solution.

Acknowledgment

T.S. thanks the Toyoda Physical and Chemical Research Institute for a Postdoctoral Fellowship.

Literature Cited

(1) Clark, R. K., Schmidt, H. H., *J. Phys. Chem.*, **69**, 3682 (1965).
(2) Cruickshank, A. J. B., Gainey, B. W., Young, C. L., *Trans. Faraday Soc.*, **64**, 337 (1968).
(3) Desty, D. M., Goldup, A., Luckhurst, G. R., Swanton, W. T., "Gas Chromatography 1962", Butterworths, London, 1962, p 67.
(4) Everett, D. H., Gainey, B. W., Young, C. L., *Trans. Faraday Soc.*, **64**, 2667 (1968).
(5) Gainey, B. W., Young, C. L., *Trans. Faraday Soc.*, **64**, 349 (1968).
(6) Hicks, C. P., Young, C. L., *Trans. Faraday Soc.*, **64**, 2675 (1968).
(7) Janini, G. M., Martire, D. E., *J. Phys. Chem.*, **78**, 1644 (1974).
(8) Liao, H.-L., Martire, D. E., Sheridan, J. P., *Anal. Chem.*, **45**, 2087 (1973).
(9) Luckhurst, G. R., Martire, D. E., *Trans. Faraday Soc.*, **65**, 1248 (1969).
(10) Martire, D. E., *Anal. Chem.*, **46**, 626 (1974).
(11) Meyer, E. F., Ross, R. A., *J. Phys. Chem.*, **75**, 831 (1971).
(12) Meyer, E. F., Stec, K. S., Hotz, R. D., *J. Phys. Chem.*, **77**, 2140 (1973).
(13) Meyer, E. F., *J. Chem. Educ.*, **50**, 191 (1973).
(14) Moelwyn-Hughes, E. A., "Physical Chemistry", 2nd ed, Pergamon Press, London, 1961, p 264.
(15) Newman, R. D., Prausnitz, J. M., *J. Phys. Chem.*, **76**, 1492 (1972).
(16) Patterson, D., Tewari, Y. B., Schreiber, H. P., *J. Chem. Soc., Faraday Trans. 2*, **68**, 885 (1972).
(17) Schreiber, H. P., Tewari, Y. B., Patterson, D., *J. Polym. Sci.*, **11**, 15 (1973).
(18) Sugiyama, T., Takeuchi, T., Suzuki, Y., *J. Chromatogr.*, **105**, 265, 273 (1975).
(19) Tewari, Y. B., Martire, D. E., Sheridan, J. P., *J. Phys. Chem.*, **74**, 2345 (1970).
(20) Tewari, Y. B., Sheridan, J. P., Martire, D. E., *J. Phys. Chem.*, **74**, 3263 (1970).
(21) Young, C. L., *Trans. Faraday Soc.*, **64**, 1537 (1968).

Received for review March 2, 1976. Accepted September 23, 1976.

Some Physicochemical Properties of Binary and Ternary Solutions of Sodium Nitrate, Ammonium Nitrate, Propylene Glycol, and Water at 25 °C

Michel Nehma, James M. Sangster, and Henry P. Schreiber*

Département du Génie Chimique, Ecole Polytechnique Campus de l'Université de Montréal, C.P. 6079, Succ. "A", Montréal, Quebec, Canada, H3C 3A7

Densities (d), relative viscosities (η/η_0), and surface tensions (γ) are reported for some binary and ternary solutions at 25 °C as follows: $NaNO_3$–propylene glycol (PG), d to saturation; NH_4NO_3–PG, d to saturation; $NaNO_3$–NH_4NO_3–H_2O, d, η/η_0, and γ near saturation; $NaNO_3$–NH_4NO_3–PG, d and η/η_0 near saturation; $NaNO_3$–H_2O–PG, d, γ, and η/η_0 at saturation; NH_4NO_3–H_2O–PG, d, η/η_0, and γ at saturation.

Foams in concentrated salt solutions, using water and mixed water/organic solvents, are becoming increasingly important in practical applications. Emphasis is therefore needed on specifying the effectiveness of surfactants in such complex media. As a prerequisite to a study of surfactant effectiveness in these media (to be reported elsewhere), we wished to determine those physicochemical solution properties which might be expected to correlate with the foaming properties of selected surfactants. Density, viscosity, and surface tension were taken to be of primary interest. The components chosen for binary and ternary solutions were relevant to applied interests; they were $NaNO_3$, NH_4NO_3, water, and propylene glycol (PG). Literature data for the desired properties are only partial and in many instances nonexistent. Accordingly in this paper we report results obtained to complement available information.

Experimental Section

$NaNO_3$ and NH_4NO_3 were Anachemia reagent grade, and were used without further purification. The solvents were PG (bp 186–187 °C, Anachemia) and distilled water. If solutions were not already clear they were filtered through paper.

Solution densities were measured by a digital densimeter Model DMA 10 (Anton Paar K.G.) which was calibrated with air and distilled water at 25 °C. Temperature was controlled by a Haake constant temperature circulator Model FS, at 25 ± 0.01 °C. The uncertainty in measured density was about $\pm 2 \times 10^{-4}$ g mL^{-1}.

Solution viscosities were measured with Cannon-Fenske viscometers in a water bath at 25 ± 0.01 °C. Flow times were reproducible to about 0.1 s, and were always greater than 100 s. No correction for kinetic effects was applied. The flow times of salt solutions were determined relative to those for the solvent in the same viscometer in each case, i.e., pure H_2O or pure PG or a mixed H_2O/PG solvent. The precision in relative viscosity η/η_0 was ±0.5%.

The surface tensions of solutions were measured by the drop-weight technique, using a relatively simple apparatus, similar to that described by Patton (*7*). A standardized experimental procedure was adopted for all measurements. The rate of drop formation was controlled by a needle-valve and was maintained between 50 and 60 s. The test liquid was kept at 25