(13) Everett, D. H., Gainey, G. W., Young, C. L., *ibid.*, **64**, 2667 (1968).
(14) Everett, D. H., Stoddart, C. T. H., *ibid.*, **57**, 746 (1961).
(15) Gainey, B. W., Young, C. L., *ibid.*, **64**, 349 (1968).
(16) Hammers, W. E., de Ligny, C. L., *Recueil*, **88**, 961 (1969).
(17) Hammers, W. E., de Ligny, C. L., *ibid.*, **90**, 819 (1971).
(18) Hammers, W. E., de Ligny, C. L., *ibid.*, p 912.
(19) Hardy, C. J., *J. Chromatogr.*, **2**, 490 (1959).
(20) Hicks, C. P., Young, C. L., *Trans. Faraday Soc.*, **64**, 2675 (1968).
(21) James, A. T., Martin, A. J. P., *Biochem. J.*, **50**, 679 (1952).
(22) James, M. R., Giddings, J. C., Keller, R. A., *J. Gas Chromatogr.*, **3**, 57 (1965).
(23) Kováts, E., *Helv. Chim. Acta*, **41**, 1915 (1958).
(24) Kudchadker, A. P., Alani, G. H., Zwolinski, B. J., *Chem. Rev.*, **68**, 659 (1969).
(25) Langer, S. H., Johnson, B. M., Conder, J. R., *J. Phys. Chem.*, **72**, 4020 (1968).
(26) Langer, S. H., Purnell, J. H., *ibid.*, **67**, 263 (1963).
(27) Littlewood, A. B., Phillips, C. S. G., Price, D. T., *J. Chem. Soc.*, **1955**, p 1480.
(28) Maffiolo, G., Lenoir, J. Y., Vidal, J., *Chim. Ind., Genie Chim.*, **104**, 1161 (1971).
(29) Martin, R. L., *Anal. Chem.*, **33**, 347 (1961).
(30) Martin, R. L., *ibid.*, **35**, 116 (1963).
(31) Martire, D. E., Blasco, P. A., Carone, P. F., Chow, L. C., Vicini, H., *J. Phys. Chem.*, **72**, 3489 (1968).
(32) Martire, D. E., Pollara, L. Z., *J. Chem. Eng. Data*, **10**, 40 (1965).
(33) Martire, D. E., Riedl, P., *J. Phys. Chem.*, **72**, 3478 (1968).
(34) McGlashan, M. L., Potter, D. J. B., *Proc. Roy. Soc., Ser. A.*, **267**, 478 (1962).
(35) Meyer, E. F., *J. Chem. Educ.*, **50**, 191 (1973).
(36) Meyer, E. F., Steck, K. S., Holte, R. D., *J. Phys. Chem.*, **77**, 2140 (1973).
(37) Pease, E. C., Thorburn, S., *J. Chromatogr.*, **30**, 344 (1967).
(38) Pecsar, R. E., Martin, J. J., *Anal. Chem.*, **38**, 1661 (1966).
(39) Petsev, N., Dimitrov, C., *J. Chromatogr.*, **20**, 15 (1965); **23**, 382 (1966).
(40) Sewell, P. A., Stock, R., *ibid.*, **50**, 10 (1970).
(41) Snyder, P. S., Thomas, J. F., *J. Chem. Eng. Data*, **13**, 527 (1968).
(42) Tewari, Y. B., Martire, D. E., Sheridan, J. P., *J. Phys. Chem.*, **74**, 2345 (1970).
(43) Wicarova, O., Novak, J., Janak, J., *J. Chromatogr.*, **65**, 241 (1972).
(44) Wilhoit, R. C., Zwolinski, B. J., "Handbook of Vapor Pressure and Heats of Vaporization of Hydrocarbons and Related Compounds," Thermodynamics Research Center, Texas A&M University, College Station, Tex., 1971.
(45) Young, C. L., *Trans. Faraday Soc.*, **64**, 1537 (1968).

Received for review March 20, 1974. Accepted December 14, 1974. Work supported by Grant No. GP-36885X from the National Science Foundation.

Activity Coefficients of Hydrochloric Acid in Several Ethylene Glycol–Water Mixtures from Emf Measurements

Utpal Sen
Department of Physical Chemistry, Jadavpur University, Calcutta 700032, India

From the electromotive force measurements of the cell of the type: Pt, H_2(gas, 1 atm); HCl(m), glycol(X), H_2O(Y); AgCl-Ag, the mean activity coefficients ($\gamma^{\pm}$) of HCl (up to $m = 1$) in several mixtures of ethylene glycol (X) and water (Y) (from 10 to 90 wt % glycol) are calculated using the standard potential (E°) values of the corresponding solvent mixtures reported earlier. As in the aqueous solutions, the activity coefficients pass through minima, but the minimum is relatively sharper with solution containing a higher percentage of glycol.

The standard potentials (E°) of the Ag–AgCl electrode in ethylene glycol and its several aqueous mixtures (10–90 wt %) at different temperatures (5–45°C) have been reported earlier from these laboratories (*4*). In the present work, these E° values have been used to calculate mean activity coefficients of hydrochloric acid in the glycol–water mixtures by extending the emf measurements of the cell

$$\text{Pt, } H_2\text{(gas, 1 atm); HCl}(m)\text{, glycol}(X)\text{, } H_2O(Y)\text{; AgCl–Ag} \tag{A}$$

containing higher concentrations of HCl in solution (up to $m = 1$).

Experimental

Preparation of electrodes, purification of solvents and other experimental details, and the apparatus used were described elsewhere (*4*). All the emf readings were corrected to 1 atm pressure of hydrogen gas.

Results and Discussion

Activity coefficients ($\gamma^{\pm}$) have been calculated from the equation:

$$\log \gamma^{\pm} = \frac{E^{\circ} - E}{2k} - \log m \tag{1}$$

where E is the observed emf value of the cell (A) containing hydrochloric acid solution of molality m. Emf measurements were carried out at 25°C with all the glycol–water mixtures up to a concentration of 1m. For 50, 70, and 90% glycol–water mixtures, measurements were also conducted at 5° and 45°C. The emf values are shown in Table I. E° values of the Ag–AgCl electrode in different solvent mixtures (*4*) used in the calculation of the activity coefficients are at the top of the emf readings in the table.

For pure glycol at concentrations of HCl higher than 0.2m, steady emf readings were not obtained, and a tendency of the emf to increase with time was observed. The readings were not reported in the present work. No such difficulty, however, was observed in working with glycol water mixtures.

The values of $\gamma^{\pm}$ at different temperatures were calculated from Equation 1 at the experimental molalities and plotted against log m on a large scale. From such plots, values of $\gamma^{\pm}$ at rounded molalities were read off and are presented in Table II. Knight and coworkers (*1, 3*) have determined the mean activity coefficients of hydrochloric acid in ethylene glycol–water mixtures (up to 60%) at 25°C. Their reported values of $\gamma^{\pm}$ of HCl appear to be slightly less ($\simeq$0.015) than the values obtained in this work. The figure shows the plot of $\gamma^{\pm}$ against the corresponding molalities for various solvents at 25°C. All individual $\gamma^{\pm}$ values for each emf reading for the solvent composition of $X = 50$ were plotted as a typical example.

The activity coefficients ($\gamma^{\pm}$) of HCl, which becomes unity at zero concentration of the electrolyte in the particular solvent under consideration, essentially constitute a measure of the interionic forces in the solvent and other effects dependent on the concentration of the solute in that medium. The activity coefficients chiefly depend upon electrostatic forces and hence the dielectric constant of the medium. The characteristic of the variation of activity coefficients with the dielectric constant may be illustrated by the results obtained with the different glycol-water mixtures as shown in the figure. The curves fall in the order of the dielectric constants of the media, the

Table I. Electromotive Force (E) of Cell (A) (in volts) (Uncertainty 0.0002 V)

	$E° = 0.2151$ V,[a]		$E° = 0.2030$ V,
m_{HCl}	$E_{25°C}$	m_{HCl}	$E_{25°C}$
10% Glycol		30% Glycol	
0.2314	0.3048	0.2093	0.2990
0.2548	0.3004	0.3232	0.2772
0.3147	0.2892	0.4092	0.2650
0.3587	0.2825	0.5278	0.2520
0.4179	0.2747	0.6387	0.2409
0.5089	0.2642	0.7771	0.2302
0.5939	0.2563	0.9042	0.2220
0.6407	0.2518	1.031	0.2134
0.7812	0.2400		
0.9426	9.2302		
1.059	0.2227		

	$E° = 0.2028$ V,	$E° = 0.1896$ V,	$E° = 0.1723$ V,
m_{HCl}	$E_{5°C}$	$E_{25°C}$	$E_{45°C}$
50% Glycol			
0.2028	0.2941	0.2887	0.2803
0.3022	0.2756	0.2690	0.2595
0.4083	0.2614	0.2538	0.2425
0.5048	0.2506	0.2425	0.2313
0.6091	0.2416	0.2326	0.2210
0.6907	0.2348	0.2256	0.2137
0.7771	0.2279	0.2188	0.2065
0.8786	0.2207	0.2113	0.1979
0.9620	0.2157	0.2063	0.1918
1.063	0.2091	0.1998	0.1854

	$E° = 0.1867$ V,	$E° = 0.1689$ V,	$E° = 0.1485$ V,
m_{HCl}	$E_{5°C}$	$E_{25°C}$	$E_{45°C}$
70% Glycol			
0.1649	0.2907	0.2816	0.2713
0.2674	0.2684	0.2583	0.2464
0.3772	0.2513	0.2403	0.2277
0.4696	0.2417	0.2305	0.2170
0.5667	0.2313	0.2196	0.2059
0.6910	0.2204	0.2082	0.1927
0.7958	0.2118	0.1994	0.1828
0.8515	0.2078	0.1951	0.1783
0.9122	0.2036	0.1901	0.1740
1.020	0.1964	0.1818	0.1665

	$E° = 0.1415$ V,	$E° = 0.1183$ V,	$E° = 0.0937$ V,
m_{HCl}	$E_{5°C}$	$E_{25°C}$	$E_{45°C}$
90% Glycol			
0.1496	0.2547	0.2419	0.2280
0.2242	0.2366	0.2234	0.2085
0.3127	0.2212	0.2037	0.1902
0.4044	0.2087	0.1937	0.1751
0.5356	0.1915	0.1760	0.1586
0.6223	0.1827	0.1672	0.1504
0.7784	0.1691	0.1532	0.1358
0.8347	0.1651	0.1490	0.1316
1.007	0.1533	0.1367	0.1191
1.085	0.1480	0.1316	0.1137

[a] $E°$ values taken from ref. *4*.

Table II. Activity Coefficient ($\gamma^{\pm}$) of HCl at Round Molalities in Glycol-Water Mixtures

	Glycol, wt %					
m_{HCl}	10	30	50	70	90	
			25°C			
0.1	0.785[a]	0.768[a]	0.745[a]	0.702[a]	0.627[a]	
0.2	0.757	0.740	0.715	0.668	0.585	
0.3	0.750	0.730	0.704	0.655	0.572	
0.4	0.749	0.728	0.702	0.647	0.577	
0.5	0.750	0.732	0.706	0.648	0.595	
0.6	0.756	0.738	0.714	0.657	0.616	
0.7	0.765	0.750	0.723	0.680	0.634	
0.8	0.773	0.761	0.734	0.698	0.655	
0.9	0.786	0.771	0.748	0.720	0.673	
1.0	0.797	0.782	0.764	0.743	0.695	
m_{HCl}	50	70	90	50	70	90
		5°C			45°C	
0.1	0.758[a]	0.722[a]	0.650[a]	0.731[a]	0.680[a]	0.600[a]
0.2	0.732	0.690	0.617	0.692	0.637	0.556
0.3	0.723	0.678	0.608	0.673	0.624	0.547
0.4	0.720	0.675	0.619	0.668	0.620	0.550
0.5	0.723	0.682	0.643	0.670	0.620	0.559
0.6	0.732	0.695	0.668	0.675	0.633	0.570
0.7	0.747	0.715	0.695	0.682	0.650	0.584
0.8	0.765	0.740	0.722	0.694	0.667	0.595
0.9	0.788	0.767	0.744	0.712	0.686	0.611
1.0	0.812	0.792	0.778	0.730	0.704	0.626

[a] Taken from ref. *4*.

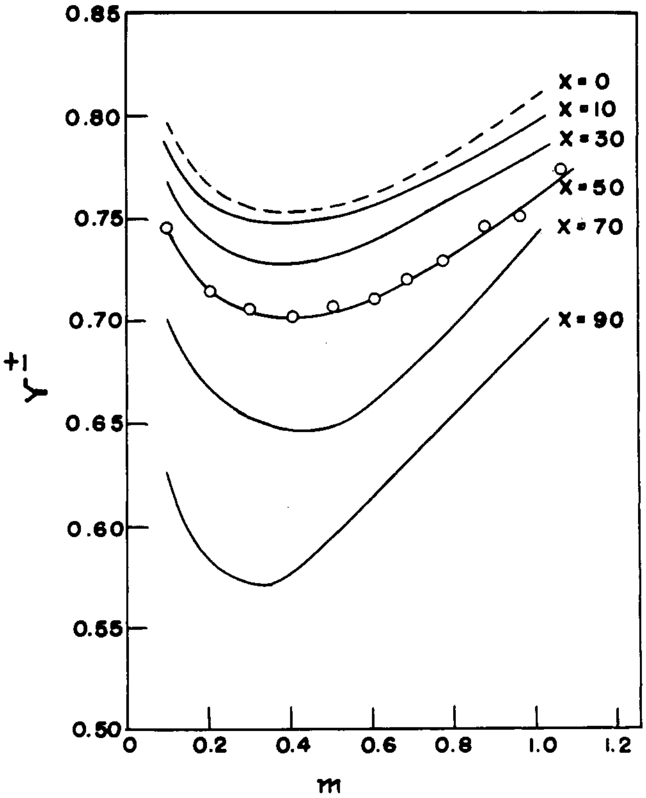

Figure 1. Activity coefficients ($\gamma^{\pm}$) of HCl at different molalities in glycol-water mixtures at 25°C. *X*, wt % of glycol

values of $\gamma^{\pm}$ at a particular molality being higher in a medium of higher dielectric constant, as expected from the Debye-Hückel equation, which essentially expresses the departure from the ideal behavior resulting from interionic electrostatic forces.

The occurrence of a minimum in the activity coefficients with increasing concentration is a general feature exhibited by electrolytes in any medium. Obviously, two opposing factors are operating, one tending to decrease and the other to increase the activity coefficient. The first factor is important at low concentrations, whereas the second one becomes predominant at higher concentrations. Apparently, a lower dielectric constant causes a relatively sharper minimum in the activity coefficient. But the dielectric constant of the medium is certainly not the determining factor. Figure 1 shows that in 90% glycol, the minimum is fairly well defined. At 25°C, this medium has nearly the same dielectric constant (43.7) as 40% dioxane. Results of the acivity coefficients of HCl in the dioxane-water mixture (*2*), however, show that even in 70% dioxane ($D = 17.7$), only a flat minimum is exhibited, which tends to become rather well defined (though less so than in 90% glycol) only when we go down to 82% dioxane ($D = 9.5$). For 0–70% glycol, the minimum occurs somewhere around 0.4*m* HCl, but at 90% glycol there appears to be a noticeable shift of the minimum toward a lower concentration. Recently (*5*), it has been seen that alkali-metal halides have minimum activity coefficients at relatively lower molalities in ethylene glycol than in water, and it has been suggested that solvation is stronger in ethylene glycol. Probably, this is also true for HCl in 90% glycol.

The activity coefficients of HCl at all concentrations decrease with increasing temperature in all the solvents. The case is similar when pure water is the solvent.

Acknowledgment

The author thanks M. N. Das and K. K. Kundu for discussions.

Literature Cited

(1) Crockford, H. D., Knight, S. B., Staton, H. A., *J. Amer. Chem. Soc.*, **72**, 2164 (1950).

(2) Harned, H. S., Owen, B. B., "The Physical Chemistry of Electrolytic Solutions," 3rd ed., Reinhold, New York, N.Y., 1958.

(3) Knight, S. B., Masi, J. F., Russel, D., *J. Amer. Chem. Soc.*, **68**, 661 (1946).

(4) Sen, U., Kundu, K. K., Das, M. N., *J. Phys. Chem.*, **71**, 3665 (1967).

(5) Sen, U., *J. Chem. Soc., Faraday I*, **69**, 2006 (1973).

Received for review March 22, 1974. Accepted December 30, 1974. Financial support by the CSIR, Government of India.

Compressibility Factors of Nitrogen-Hydrogen Sulfide Mixtures

Donald B. Robinson,[1] Gerald P. Hamaliuk,[2] Thamra R. Krishnan, and P. Raj Bishnoi[3]

Department of Chemical Engineering, The University of Alberta, Edmonton, Alta., Canada

Experimental compressibility factors were determined for two gas mixtures, one containing 8.6 mol % hydrogen sulfide and 91.4 mol % nitrogen and the other containing 22.2 mol % hydrogen sulfide, 76.5 mol % nitrogen, and 1.3 mol % carbon dioxide. Measurements were made at 20°, 40°, 60°, 80°, and 100°C at pressures to about 4500 psia. Second virial coefficients were calculated for both mixtures at each temperature. The experimental compressibility factors were compared with those calculated with the Benedict-Webb-Rubin equation of state. The root-mean-square difference was 0.81% for the 8.6 mol % mixture and 0.62% for the 22.2 mol % mixture.

The work reported in this paper represents part of a continuing study on the properties and phase behavior of binary systems containing hydrocarbons and related nonhydrocarbons. During the course of the study, it became increasingly evident that sets of independent experimental measurements on properties such as density, heat capacity, and equilibrium-phase compositions would be extremely helpful in equation-of-state development, parameter estimating, and related correlation efforts. Accordingly, a series of such measurements has been made on the equilibrium-phase properties of mixtures of nitrogen and hydrogen sulfide at five temperatures and up to 3000 psia, on the heat capacity of two mixtures of nitrogen and hydrogen sulfide at three temperatures and pressures to 2350 psia, and on the density of the same two mixtures at five temperatures and pressures to about 4500 psia. The density measurements are the subject of this paper.

Experimental Method

The experimental method used in this work was based on that proposed in 1936 by Burnett (*3*). Briefly, it consists of expanding the gas under investigation from a high-pressure chamber into an evacuated chamber at constant temperature and then successively continuing the expansions until a low enough pressure has been reached so that extrapolations can be made to zero pressure.

The experimental routine commences by filling chamber 1 to an initial pressure P_0. Chamber 2 is then evacuated, the temperature of the combined system is allowed to equilibrate, and the gas is expanded through a constant volume valve so that both chambers are filled. When the constant temperature has been restored, the pressure is measured, the constant volume valve is closed, and chamber 2 is again evacuated. This sequence is repeated so that a series of pressures, P_0, P_1, . . . P_{j-1}, P_j, is obtained for each experimental run at the chosen temperature.

The details of this procedure and the derivation of the equations necessary for determining the cell constant, the run constant, and the compressibility factor at each pressure have been presented by other workers (*3*, *4*, *6*).

---

[1] To whom correspondence should be addressed.

[2] Present address, Celanese Canada Ltd., Edmonton, Alta., Canada.

[3] Present address, Fluor Canada Ltd., Calgary, Alta., Canada.