from a regression line was 0.000 to 0.004 cp, the maximum possible relative deviation being less than 1%. As expected, the fit of the viscosity data to an Arrhenius equation is better than for the diffusion data, the viscosity data being from a more precise measurement technique.

## DISCUSSION

The viscosity and diffusion data of Table I are plotted in Figures 1 and 2, respectively. These activation energies and entropies vary nonlinearly throughout the concentration range. Although the appearance of these plots cannot at present be rationalized, these complexities are not surprising, as the solution environment is being severely altered (at 7*M* urea there are about eight water molecules per one urea molecule). These results are of interest, since precise measurements of refractive indices at a single temperature did not show a concentration dependence *(10)* and it was concluded that urea solutions do not undergo a detectable transition in structure at some critical concentration of urea. The inflections and discontinuities of Figures 1 and 2 suggest some transition in structure that affects differently the temperature dependence of these two transport properties, although the Stokes-Einstein relationship (Table I) is apparently not affected.

These findings, as previously suggested *(9)*, should be relevant to protein thermodynamics and protein denaturation.

## ACKNOWLEDGMENT

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# Thermodynamics of Hydrochloric Acid in 8.03, 20.76, 44.04, 70.28, and 87.71 Weight % 2-Propanol–Water Mixtures from E.M.F. Measurements at 0°, 15°, 25°, and 35°C

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**The electromotive force measurements of the cell, Pt, $H_2$ (1 atm) | HCl (*m*), 2-propanol (*X*), water (*Y*) | AgCl, Ag were made for 8.03, 20.76, 44.04, 70.28, and 87.71 weight % 2-propanol at 0°, 15°, 25°, and 35° C. The cell was used to derive the standard e.m.f. of this cell for 2-propanol–water mixtures by using a polynomial curve-fitting technique, the mean activity coefficient of hydrochloric acid, the primary and secondary medium effects, the relative partial molal heat content and heat capacity of HCl, and the means of converting the values obtained from the mixed-solvent systems to those of the standard reference aqueous state. The curve-fitting program permits evaluation of the standard potential in mixed solvents, with elimination of some of the uncertainties encountered in the conventional linear graphical extrapolations where previous knowledge of the dielectric constant of the solvent, density of the mixed-solvent, and the ion-size parameter is required. The molality of HCl ranged from 0.1 to 0.001 mole kg$^{-1}$.**

The properties of hydrochloric acid in aqueous-organic mixed solvents *(3-5, 7-11)* has long been a subject of interest. The normal graphical extrapolation *(3, 4, 7-9)* of the e.m.f. data of the cell Pt, $H_2$ (1 atm) | HCl (*m*), 2-propanol (*X*), water (*Y*) | AgCl, Ag, using Gronwall, LaMer, and Sandved's *(5)* extension of the Debye-Hückel theory usually exhibits errors and shows curvatures at the lower concentration, which is the region of greatest importance. The work reported here was undertaken to eliminate the errors encountered in the linear graphical extrapolations for the determination of $E^0$ and to interpret the e.m.f. data of hydrochloric acid in a medium of varying dielectric constant.

The binary 2-propanol-water solvent mixture of various compositions was chosen. These media are common laboratory solvents, and as such are used in the investigations of the acid-base properties of compounds that are not very soluble in water.

The scope of the investigation can be summarized as follows. The standard e.m.f. of the cell was evaluated by a polynomial curve-fitting technique. The mean activity coefficients, primary and secondary medium effects, relative

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partial molal heat contents, and relative partial molal heat capacities for hydrochloric acid were derived. A means of converting the values obtained from the mixed solvent systems to those of the standard reference aqueous state, adapted to computer techniques, was devised.

The linear graphical extrapolation requires knowledge of the bulk dielectric constant, whereas this information is not necessary when the extrapolation is made by a polynomial curve-fitting program. In previous papers (*12–15*), it was reported that the rearranged Nernst equation containing extended terms of the Debye-Hückel theory may be expressed as a polynomial in powers of $m^{1/2}$ and the ion-size parameter is reasonably constant as long as the concentration of hydrochloric acid is low and the bulk dielectric constant of the solvent is not less than 18.

Harned and coworkers (*7*) have reported e.m.f. measurements on hydrochloric acid for 10% 2-propanol–water mixtures at 25° C. This paper describes the behavior and accurate measurements of the thermodynamic properties of hydrochloric acid in 8.03, 20.76, 44.04, 70.28, and 87.71 weight % 2-propanol at 0°, 15°, 25°, and 35° C. The molality, *m*, of hydrochloric acid ranged from 0.1 to 0.001 mole $\text{kg}^{-1}$.

## EXPERIMENTAL

Hydrochloric acid used in all preparations of the solutions was prepared from reagent grade acid by distilling twice in all-glass apparatus; each time only the middle fraction was collected. The stock solution was standardized volumetrically with $Na_2CO_3$, and gravimetrically with $AgNO_3$ weighed as AgCl. The water used for all preparations had a conductivity less than $1 \times 10^{-6}$ mho $\text{cm}^{-1}$. Commercially available spectrophotometric grade 2-propanol was obtained from the Mallinckrodt Chemical Works. Its purity was checked by chromatography.

The preparation of electrodes, the design of the cells, the purification of hydrogen gas, and the preparation of the solutions have been discussed (*1, 12, 13*). The molality of the acid in all the solutions reported may be relied upon within ±0.05%.

Nine different solutions of hydrochloric acid in mixed solvents (in the concentration range of 0.1 to 0.001 mole $\text{kg}^{-1}$) were prepared. The weight per cent of the mixed solvent was calculated from the appropriate volume and density data. Five systems—8.03, 20.76, 44.04, 70.28, and 87.71 weight % 2-propanol—were studied at 0°, 15°, 25°, and 35° with a precision of ±0.01° C in the Sargent Thermonitor-controlled water bath. The isopropyl alcohol contents of the solutions are correct to within 0.05%.

Pure hydrogen gas saturated with the solution vapor was passed through the cell solution until equilibrium was reached, assumed to be when e.m.f. measurements taken by means of a Leeds & Northrup K-3 Universal Type potentiometer over a period of one-half hour agreed to ±0.05 mv. The system reached equilibrium a bit faster at higher temperature.

Two silver-silver chloride electrodes and two hydrogen electrodes were used. The vapor pressure data of water and 2-propanol, needed to correct the hydrogen pressure to 1 atm ($101{,}325 N\,m^{-2}$), were obtained from the Handbook of Chemistry and Physics (*6*). By the method of least squares, the vapor pressure data at the experimental temperatures were taken directly from the computer.

## RESULTS

The e.m.f. data listed in Table I are equal to *E*, the potential of the cell corrected to a hydrogen pressure of 1 atm. Each e.m.f. value represents the average value of four readings for each molality of hydrochloric acid at the same temperature. All four values agreed within 0.00005 volt. Typically, the lowest and highest e.m.f. values for replicate cells differed by 0.00014 volt.

Plots of the dependent variable $E'$ $[=E + (2RT/F) \ln m]$ against $m^{1/2}$ are presented in Figure 1, in which the experimental points are represented by circles, whereas the solid lines are the calculated plots using the parameters of Equation 3 evaluated from the experimental data. Figure 1 shows that the theoretical curve for system I at 0° C is consistently above that of the experimental data even in dilute solutions. This is in good agreement with the author's previous investigations (*13*).

Table I. Electromotive Force $E|V$ of Cell Pt, $H_2$ (1 Atm)|HCl (*m*), 2-Propanol (*X*), Water (*Y*)|AgCl, Ag at 0°, 15°, 25°, and 35° C

| $m$\|Mole $\text{Kg}^{-1}$ | *E* | | | |
|---|---|---|---|---|
| | 0° C | 15° C | 25° C | 35° C |
| $X =$ 8.03 weight % 2-Propanol | | | | |
| 0.10276 | 0.34643 | 0.34649 | 0.34536 | 0.34356 |
| 0.08218 | 0.35626 | 0.35692 | 0.35627 | 0.35428 |
| 0.06143 | 0.36844 | 0.36901 | 0.36922 | 0.36828 |
| 0.04093 | 0.38768 | 0.38992 | 0.39026 | 0.38947 |
| 0.02057 | 0.41728 | 0.42085 | 0.42268 | 0.42335 |
| 0.01036 | 0.44720 | 0.45323 | 0.45591 | 0.45769 |
| 0.00512 | 0.47947 | 0.48647 | 0.48985 | 0.49255 |
| 0.00306 | 0.50361 | 0.51168 | 0.51637 | 0.52006 |
| 0.00102 | 0.55007 | 0.56043 | 0.56621 | 0.57187 |
| $X =$ 20.76 Weight % 2-Propanol | | | | |
| 0.10627 | 0.33412 | 0.33632 | 0.33556 | 0.33398 |
| 0.08498 | 0.34480 | 0.34708 | 0.34697 | 0.34519 |
| 0.06352 | 0.35741 | 0.36065 | 0.36079 | 0.35988 |
| 0.04251 | 0.37513 | 0.37805 | 0.37934 | 0.37838 |
| 0.02134 | 0.40582 | 0.41122 | 0.41313 | 0.41404 |
| 0.01071 | 0.43598 | 0.44325 | 0.44642 | 0.44794 |
| 0.00530 | 0.46771 | 0.47652 | 0.48072 | 0.48309 |
| 0.00317 | 0.49010 | 0.50014 | 0.50545 | 0.50871 |
| 0.00106 | 0.53721 | 0.54909 | 0.55567 | 0.56064 |
| $X =$ 44.04 Weight % 2-Propanol | | | | |
| 0.11268 | 0.31740 | 0.31598 | 0.31274 | 0.30878 |
| 0.09203 | 0.33519 | 0.33348 | 0.33075 | 0.32669 |
| 0.06751 | 0.34772 | 0.34702 | 0.34431 | 0.34098 |
| 0.04488 | 0.36645 | 0.36580 | 0.36405 | 0.36079 |
| 0.02260 | 0.39520 | 0.39429 | 0.39251 | 0.39110 |
| 0.01136 | 0.42486 | 0.42741 | 0.42750 | 0.42638 |
| 0.00585 | 0.45334 | 0.45751 | 0.45821 | 0.45796 |
| 0.00366 | 0.47561 | 0.47990 | 0.48185 | 0.48254 |
| 0.00112 | 0.52215 | 0.52981 | 0.53338 | 0.53559 |
| $X =$ 70.28 Weight % 2-Propanol | | | | |
| 0.11986 | 0.30243 | 0.29520 | 0.28749 | 0.27961 |
| 0.09555 | 0.31485 | 0.30675 | 0.30171 | 0.29543 |
| 0.07184 | 0.32270 | 0.31605 | 0.31042 | 0.30354 |
| 0.04775 | 0.33880 | 0.33290 | 0.32678 | 0.32000 |
| 0.02399 | 0.36604 | 0.36104 | 0.35505 | 0.34874 |
| 0.01201 | 0.39316 | 0.38922 | 0.38523 | 0.37913 |
| 0.00597 | 0.42202 | 0.41944 | 0.41575 | 0.41099 |
| 0.00360 | 0.44249 | 0.44068 | 0.43861 | 0.43515 |
| 0.00119 | 0.48667 | 0.48674 | 0.48557 | 0.48303 |
| $X =$ 87.71 Weight % 2-Propanol | | | | |
| 0.12465 | 0.26538 | 0.25274 | 0.24152 | 0.23006 |
| 0.09938 | 0.27252 | 0.25976 | 0.24940 | 0.23898 |
| 0.07471 | 0.28385 | 0.27139 | 0.26142 | 0.24864 |
| 0.04966 | 0.29734 | 0.28571 | 0.27619 | 0.26437 |
| 0.02495 | 0.32317 | 0.31149 | 0.30233 | 0.29210 |
| 0.01249 | 0.34823 | 0.33740 | 0.32743 | 0.31686 |
| 0.00620 | 0.37751 | 0.36800 | 0.35966 | 0.34916 |
| 0.00374 | 0.39709 | 0.38839 | 0.38060 | 0.37148 |
| 0.00130 | 0.44318 | 0.43599 | 0.43024 | 0.42259 |

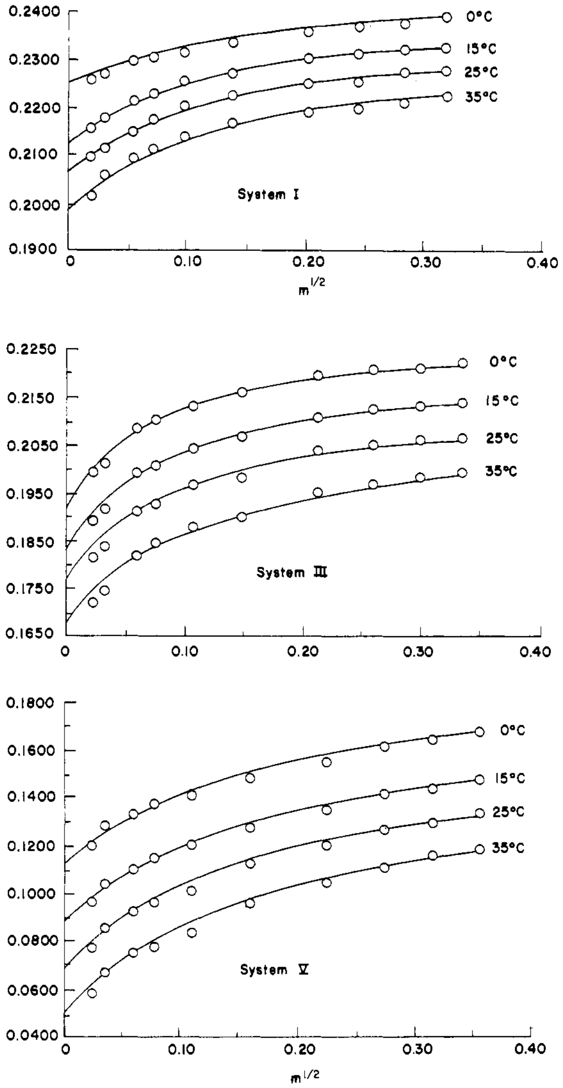

Figure 1. Plots of $E'$ vs. $m^{1/2}$, $E' = E + [(2RT/F) \ln m]$

0 Experimental points
– Theoretical curves
System I. 8.03 weight % 2-propanol
System III. 44.04 weight % 2-propanol
System V. 87.71 weight % 2-propanol

Table II. Standard Potentials ($E^\circ$) of Cell Pt, $H_2$ (1 Atm)| HCl ($m$), 2-Propanol ($X$), Water ($Y$)| AgCl, Ag

($X$ and $Y$ are weight percentages)

| | $\theta$ °C | | | |
|---|---|---|---|---|
| $X$ | 0° C | 15° C | 25° C | 35° C |
| 0.0 | 0.23655 | 0.22857 | 0.22234 | 0.21565 |
| 8.03 | 0.22591 | 0.21116 | 0.20522 | 0.19793 |
| 20.76 | 0.20831 | 0.20178 | 0.19517 | 0.18772 |
| 44.04 | 0.19623 | 0.18560 | 0.17831 | 0.16831 |
| 70.28 | 0.16176 | 0.14208 | 0.12987 | 0.11586 |
| 87.71 | 0.11657 | 0.09128 | 0.07253 | 0.05177 |

Examination of Figure 1 for $x = 8.03$ and 44.04 shows that the curvature becomes more pronounced, particularly at the lower concentration range of HCl acid, as the concentration of 2-propanol is increased. This curved segment of the plot is, unfortunately, the region of greatest importance and involves error in linear graphical extrapolations. The curve-fitting technique permits evaluation of the standard potential in mixed solvents with elimination of some of the errors encountered in the conventional linear graphical extrapolations, where previous knowledge of the dielectric constant of the solvent and the ion-size parameter is required. This information is not required in a polynomial curve-fitting technique.

## STANDARD E.M.F. AND THERMODYNAMIC CONSTANTS

The rearranged Nernst equation may be written

$$E + (2RT/F) \ln m = E^\circ - (2RT/F) \ln \gamma_\pm \qquad (1)$$

in which $E$ is the potential of the cell corrected to a hydrogen pressure of 1 atm, and $m$ and $\gamma_\pm$ are the molality and mean activity coefficient of hydrochloric acid in the medium under investigation. A plot of the left side of Equation 1 against some function of molality is obviously nonlinear. The polynomial curve-fitting technique is used to eliminate the error encountered in normal graphical extrapolations and is based on the assumption that a set of experimental data can be best fitted to a polynomial of the form

$$y = A_0 + A_1x + A_2x^2 + \ldots\ldots A_{15}x^{15} \qquad (2)$$

The quantity $[E + (2RT/F) \ln m]$ in Equation 1 may be expressed as a polynomial series in $m^{1/2}$ of the form (*15*) which is further corroborated by Dill *et al.* (*2*)

$$E + (2RT/F) \ln m = E^\circ + A_1m^{1/2} + A_2m + A_3m^{3/2} + \ldots\ldots \qquad (3)$$

in which coefficients $E^\circ$, $A_1$, etc., are not arbitrary constants. The proof (*15*) is based on the assumption and the validity of the Debye-Hückel theory. The polynomial curve-fitting technique simply avoids the numerical computation of the Gronwall, LaMer, and Sandved (*5*) extension of the Debye-Hückel equation (*3*). It is evident from Equation 2 that the first approximation is of linear form, $Y = A_0 + A_1x$. The third-degree equation was used for the investigations of 8.03, 20.76, 44.04, 70.28, and 87.71 weight % 2-propanol. There was a direct correlation between the degree of equation (*15*) and the dielectric constant of the solvent.

The standard error calculated by the method of least squares and the general nature of the curves obtained by plotting the experimental quantity $E'$ $[E' = E + (2RT/F) \ln m]$ against $m^{1/2}$ were the important criteria in deciding the degree of equation to use. The program calculated the appropriate coefficients for the degree of equation specified, the standard error, and the calculated value of the dependent variable, $E'$.

The mean activity coefficients of hydrochloric acid in 2-propanol–water mixtures have been calculated from the following rearranged Nernst equation and are given in Table III.

$$\ln \gamma_\pm = \frac{{}^{s}E^\circ_m - [{}^{s}E + (2RT/F) \ln m]}{(2RT/F)} \qquad (4)$$

in which ${}^{s}E^\circ_m$ corresponds to $E^\circ$, which is the standard potential in the mixed solvents. ${}^{s}E$ corresponds to $E$ (*9*).

To discuss the influence of the solvent medium upon the numerical values of the ionization constant of an ionized solute and the activity coefficient, the total medium effect, which is the summation of the primary and the secondary medium effects, is considered.

The primary medium effect is defined as the difference between the solution energies in two different solvents and is independent of the solute concentration. The effect (log ${}^{s}_{w}\gamma^\circ_\pm$ HCl) of 2-propanol–water mixtures was calculated from Equation 5 (Table IV).

$$({}^{w}E^\circ_m - {}^{s}E^\circ_m) = \underset{m \to 0}{Lt} [(4.606RT/F) \log {}^{s}_{w}\gamma_\pm] = (4.606RT/F) \log {}^{s}_{w}\gamma^\circ_\pm \qquad (5)$$

### Table III. Mean Activity Coefficients of Hydrochloric Acid in 2-Propanol–Water Mixture at Various Temperatures[a]

| $m$, (HCl)\| Mole Kg$^{-1}$ | 0° C | 15° C | 25° C | 35° C |
|---|---|---|---|---|
| | $X$ = 0[b] Weight % 2-Propanol | | | |
| 0.1 | 0.802 | 0.800 | 0.796 | 0.791 |
| 0.05 | 0.834 | 0.832 | 0.830 | 0.826 |
| 0.02 | 0.877 | 0.877 | 0.875 | 0.873 |
| 0.01 | 0.906 | 0.905 | 0.904 | 0.902 |
| 0.005 | 0.930 | 0.929 | 0.928 | 0.926 |
| 0.002 | 0.954 | 0.953 | 0.952 | 0.951 |
| 0.001 | 0.966 | 0.966 | 0.965 | 0.964 |
| | $X$ = 8.03 Weight % 2-Propanol | | | |
| 0.1 | 0.756 | 0.635 | 0.633 | 0.625 |
| 0.05 | 0.785 | 0.676 | 0.670 | 0.664 |
| 0.02 | 0.839 | 0.694 | 0.691 | 0.683 |
| 0.01 | 0.877 | 0.727 | 0.725 | 0.716 |
| 0.005 | 0.908 | 0.769 | 0.769 | 0.760 |
| 0.002 | 0.939 | 0.828 | 0.828 | 0.821 |
| 0.001 | 0.956 | 0.867 | 0.867 | 0.862 |
| | $X$ = 20.76 Weight % 2-Propanol | | | |
| 0.1 | 0.647 | 0.625 | 0.610 | 0.599 |
| 0.05 | 0.672 | 0.659 | 0.641 | 0.633 |
| 0.02 | 0.698 | 0.682 | 0.661 | 0.653 |
| 0.01 | 0.735 | 0.718 | 0.698 | 0.690 |
| 0.005 | 0.780 | 0.764 | 0.745 | 0.739 |
| 0.002 | 0.838 | 0.825 | 0.810 | 0.805 |
| 0.001 | 0.876 | 0.865 | 0.853 | 0.849 |
| | $X$ = 44.04 Weight % 2-Propanol | | | |
| 0.1 | 0.620 | 0.605 | 0.611 | 0.597 |
| 0.05 | 0.595 | 0.581 | 0.592 | 0.583 |
| 0.02 | 0.655 | 0.629 | 0.647 | 0.637 |
| 0.01 | 0.718 | 0.688 | 0.707 | 0.697 |
| 0.005 | 0.772 | 0.767 | 0.759 | 0.758 |
| 0.002 | 0.846 | 0.836 | 0.829 | 0.822 |
| 0.001 | 0.885 | 0.879 | 0.877 | 0.872 |
| | $X$ = 70.28 Weight % 2-Propanol | | | |
| 0.1 | 0.424 | 0.391 | 0.389 | 0.379 |
| 0.05 | 0.475 | 0.440 | 0.439 | 0.432 |
| 0.02 | 0.555 | 0.526 | 0.524 | 0.524 |
| 0.01 | 0.626 | 0.599 | 0.599 | 0.598 |
| 0.005 | 0.697 | 0.676 | 0.675 | 0.674 |
| 0.002 | 0.782 | 0.768 | 0.766 | 0.762 |
| 0.001 | 0.835 | 0.822 | 0.822 | 0.822 |
| | $X$ = 87.71 Weight % 2-Propanol | | | |
| 0.1 | 0.364 | 0.335 | 0.319 | 0.300 |
| 0.05 | 0.428 | 0.400 | 0.382 | 0.366 |
| 0.02 | 0.515 | 0.492 | 0.478 | 0.462 |
| 0.01 | 0.590 | 0.571 | 0.561 | 0.544 |
| 0.005 | 0.666 | 0.651 | 0.644 | 0.629 |
| 0.002 | 0.758 | 0.747 | 0.743 | 0.730 |
| 0.001 | 0.816 | 0.807 | 0.805 | 0.794 |

[a] Accuracy of molality within 0.05%. [b] Data from Harned and Owen (9).

### Table IV. Primary Medium Effect (Log $^{s}_{w}\gamma^{\circ}_{\pm}$ HCl) of 2-Propanol–Water Mixtures upon Hydrochloric Acid at Four Temperatures

($X$ = weight % 2-propanol)

| $X$ | 0° C | 15° C | 25° C | 35° C |
|---|---|---|---|---|
| 8.03 | 0.0980 | 0.1521 | 0.1446 | 0.1448 |
| 20.76 | 0.2604 | 0.2342 | 0.2295 | 0.2283 |
| 44.04 | 0.3718 | 0.3756 | 0.3720 | 0.3870 |
| 70.28 | 0.6898 | 0.7562 | 0.7813 | 0.8158 |
| 87.71 | 1.1066 | 1.2003 | 1.2659 | 1.3398 |

where $^{w}E^{\circ}_{m}$ is the standard potential of the cell in aqueous medium relative to unit value at infinite dilution in pure water—that is, $^{w}_{w}\gamma_{\pm} \rightarrow 1$ as $m \rightarrow 0$. $\underset{m \rightarrow 0}{Lt}\ ^{s}_{w}\gamma_{\pm}$ represents the mean activity coefficient of hydrochloric acid at infinite dilution (zero molality) in a mixed solvent referred to unity at infinite dilution in aqueous state.

The secondary medium effect is always given by the difference between the total and primary effects. It is defined as due to the difference in ion-ion interaction in two different solvents and is, of course, concentration-dependent.

It is represented thermodynamically as

$$\ln \frac{^{s}_{w}\gamma_{\pm}}{^{w}_{w}\gamma_{\pm}} = \underset{m \rightarrow 0}{Lt} (\ln {^{s}_{w}\gamma_{\pm}}) + \ln \frac{^{s}_{s}\gamma_{\pm}}{^{w}_{w}\gamma_{\pm}} \quad (6)$$

in which superscripts $w$ and $s$ indicate that the measurements are carried out in water and in a mixed solvent, respectively. Subscripts $w$ and $s$ on the mean activity coefficients ($\gamma_{\pm}$) show that $\gamma_{\pm}$ is measured relative to unit value at infinite dilution in water and in a mixed solvent, respectively. The term $^{s}_{s}\gamma_{\pm}$ measures the difference in the "nonideal" part of the chemical potential of the HCl acid at finite concentration and at infinite dilution of the mixed solvent. The left-hand term of Equation 6 is the total medium effect and the extreme right-hand term is the secondary medium effect, the values of which are summarized in Table V.

The relative partial molal heat content, $\bar{L}_2$, and the relative partial molal heat capacity, $\bar{J}_2$, are defined as the difference between the partial molal property in a given solution and its value in the reference state—i.e., relative to infinite dilution of the solvent.

$\bar{L}_2$ can be computed from the equation

$$\bar{L}_2 = F(a - a_0) + F(c - c_0)T^2 \quad (7)$$

in which $T$ represents the absolute temperature in degrees Kelvin and constants $a$, $a_0$, etc., can be determined by the method of least squares from the e.m.f. data at various temperatures from the equations

$$^{s}E = a + bT + cT^2 \quad (8)$$

$$^{s}E^{\circ} = a_0 + b_0T + c_0T^2 \quad (9)$$

The relative partial molal heat capacity, $\bar{J}_2$, of hydrochloric acid in a mixed solvent can be calculated from the equation

$$\bar{J}_2 = 2F(c - c_0)T \quad (10)$$

in which coefficients $c$, $c_0$, etc., are easily determined by the method of least squares (Tables VI and VII). The values of $\bar{L}_2$ and $\bar{J}_2$ are given in Table VIII.

## DISCUSSION

In previous papers (*13, 15*), it was reported that the polynomial curve-fitting technique yields values of the standard potentials, $E^{\circ}$, in excellent agreement with the best values of $E^{\circ}$ obtained by linear extrapolation. To verify this, the published data of well known investigators were used. The values of $E^{\circ}$ given in Table II can be considered correct to ±0.06 mv for $X$ = 8.03, 20.76, and 44.04; for $X$ = 70.28 and 87.71 the errors are estimated to be ±0.1 and ±0.3 mv, respectively.

A thorough examination of the data for the mean activity coefficients of hydrochloric acid (Table III) shows that

Table V. Secondary Medium Effect of 2-Propanol–Water Mixtures upon Hydrochloric Acid at Various Temperatures[a]

| $m$/ Mole Kg$^{-1}$ | 0° C | 15° C | 25° C | 35° C |
|---|---|---|---|---|
| $X$ = 8.03 Weight % 2-Propanol | | | | |
| 0.1 | −0.2847 | −0.5805 | −0.5614 | −0.5689 |
| 0.05 | −0.2870 | −0.5581 | −0.5466 | −0.5511 |
| 0.02 | −0.2699 | −0.5833 | −0.5694 | −0.5790 |
| 0.01 | −0.2582 | −0.5700 | −0.5543 | −0.5645 |
| 0.005 | −0.2491 | −0.5392 | −0.5214 | −0.5311 |
| 0.002 | −0.2409 | −0.4906 | −0.4722 | −0.4804 |
| 0.001 | −0.2365 | −0.4578 | −0.4396 | −0.4459 |
| $X$ = 20.76 Weight % 2-Propanol | | | | |
| 0.1 | −0.8140 | −0.7851 | −0.7946 | −0.8044 |
| 0.05 | −0.8163 | −0.7725 | −0.7870 | −0.7920 |
| 0.02 | −0.8284 | −0.7898 | −0.8090 | −0.8151 |
| 0.01 | −0.8088 | −0.7702 | −0.7879 | −0.7931 |
| 0.005 | −0.7754 | −0.7351 | −0.7478 | −0.7520 |
| 0.002 | −0.7286 | −0.6831 | −0.6896 | −0.6925 |
| 0.001 | −0.6975 | −0.6490 | −0.6516 | −0.6528 |
| $X$ = 44.04 Weight % 2-Propanol | | | | |
| 0.1 | −1.0978 | −1.1442 | −1.1211 | −1.1727 |
| 0.05 | −1.2074 | −1.2250 | −1.1942 | −1.2397 |
| 0.02 | −1.1867 | −1.1962 | −1.1591 | −1.2056 |
| 0.01 | −1.1311 | −1.1387 | −1.1032 | −1.1486 |
| 0.005 | −1.0718 | −1.0798 | −1.0473 | −1.0913 |
| 0.002 | −1.0051 | −1.0127 | −0.9864 | −1.0285 |
| 0.001 | −0.9660 | −0.9741 | −0.9522 | −0.9922 |
| $X$ = 70.28 Weight % 2-Propanol | | | | |
| 0.1 | −2.2258 | −2.4562 | −2.5151 | −2.6136 |
| 0.05 | −2.1512 | −2.3774 | −2.4350 | −2.5255 |
| 0.02 | −2.0460 | −2.2707 | −2.3122 | −2.3883 |
| 0.01 | −1.9588 | −2.1741 | −2.1174 | −2.2813 |
| 0.005 | −1.8767 | −2.0810 | −2.1174 | −2.1865 |
| 0.002 | −1.7872 | −1.9764 | −2.0166 | −2.0875 |
| 0.001 | −1.7351 | −1.9155 | −1.9595 | −2.0316 |
| $X$ = 87.71 Weight % 2-Propanol | | | | |
| 0.1 | −3.3379 | −3.6341 | −3.8282 | −4.0540 |
| 0.05 | −3.2160 | −3.4966 | −3.6910 | −3.8998 |
| 0.02 | −3.0808 | −3.3418 | −3.5190 | −3.7220 |
| 0.01 | −2.9772 | −3.2251 | −3.3924 | −3.5901 |
| 0.005 | −2.8814 | −3.1205 | −3.2803 | −3.4731 |
| 0.002 | −2.7777 | −3.0078 | −3.1528 | −3.3496 |
| 0.001 | −2.7176 | −2.9436 | −3.0970 | −3.2794 |

[a] Accuracy of molality within 0.05%.

in a given system and at a given temperature, the increase in the value of the mean activity coefficient corresponds to the decrease in the molality of hydrochloric acid. The activity coefficients at all concentrations and temperatures decrease with increasing temperature. The general pattern of our results (2-propanol-water) are in good agreement with those obtained by Roy and Sen (*13, 15*) and those of Harned and his coworkers in other mixed solvents (*9–11*). According to Harned and Owen (*9*), an error of ±0.05 mv in the measured values of the electromotive force corresponds to an error of 0.001 in the values of the mean activity coefficient. This seems to be the case in this investigation.

There is no appreciable ionic association for $X$ = 8.03. From Figure 1 and the activity coefficient data it is found that for 20.76 and 44.04 weight % 2-propanol, there is evidence, though barely noticeable, of ionic associations or interactions that appear to be present to a considerable extent for $X$ = 70.28. Hydrochloric acid shows the characteristic behavior of a weak electrolyte for $X$ = 87.71, where ion pairing is favored by the relatively low dielectric constant of the solvent.

Table VI. Coefficients of Equation $E = a + bT + cT^2$[a]

| $m$/ Mole Kg$^{-1}$ | $a \times 10^2$ | $b \times 10^3$ | $c \times 10^6$ | S.D. |
|---|---|---|---|---|
| $X$ = 8.03 Weight % 2-Propanol | | | | |
| 0.1 | −5.8038 | 2.8598 | −5.0351 | 0.0000 |
| 0.05 | 10.814 | 1.8534 | −3.1645 | 0.0001 |
| 0.02 | −10.542 | 3.4254 | −5.5194 | 0.0001 |
| 0.01 | −15.491 | 3.8838 | −6.1260 | 0.0000 |
| 0.002 | 18.954 | 1.8579 | −2.3553 | 0.0001 |
| 0.001 | 43.434 | 0.3233 | 0.4089 | 0.0002 |
| $X$ = 20.76 Weight % 2-Propanol | | | | |
| 0.1 | −22.629 | 3.8911 | −6.6929 | 0.0001 |
| 0.05 | −14.948 | 3.4959 | −5.8616 | 0.0001 |
| 0.02 | −19.451 | 3.9492 | −6.3639 | 0.0001 |
| 0.01 | −17.054 | 3.8985 | −6.0944 | 0.0001 |
| 0.002 | −22.179 | 4.5382 | −6.8175 | 0.0000 |
| 0.001 | −24.270 | 4.8078 | −7.1149 | 0.0000 |
| $X$ = 44.04 Weight % 2-Propanol | | | | |
| 0.1 | −14.827 | 3.4925 | −6.4239 | 0.0001 |
| 0.05 | 1.7722 | 2.5396 | −4.6777 | 0.0001 |
| 0.02 | −0.9623 | 2.8995 | −5.0964 | 0.0000 |
| 0.01 | −1.8083 | 3.0642 | −5.2048 | 0.0000 |
| 0.002 | 1.0328 | 3.1059 | −4.8341 | 0.0001 |
| 0.001 | −5.6430 | 3.6731 | −5.6128 | 0.0001 |
| $X$ = 70.28 Weight % 2-Propanol | | | | |
| 0.1 | 11.038 | 1.9128 | −4.3198 | 0.0000 |
| 0.05 | 3.1362 | 2.5805 | −5.3406 | 0.0000 |
| 0.02 | −6.1671 | 3.4058 | −6.6333 | 0.0001 |
| 0.01 | −8.5844 | 3.6984 | −7.0195 | 0.0000 |
| 0.002 | 9.3182 | 2.7302 | −4.9997 | 0.0000 |
| 0.001 | 16.958 | 2.3154 | −4.1096 | 0.0001 |
| $X$ = 87.71 Weight % 2-Propanol | | | | |
| 0.1 | 1.3834 | 2.6639 | −6.2842 | 0.0001 |
| 0.05 | −3.8098 | 3.1592 | −7.0664 | 0.0001 |
| 0.02 | −0.7903 | 3.1425 | −6.9489 | 0.0000 |
| 0.01 | −1.3744 | 3.3184 | −7.1635 | 0.0000 |
| 0.002 | −3.7903 | 3.7766 | −7.6601 | 0.0000 |
| 0.001 | 4.7638 | 3.3072 | −6.6953 | 0.0001 |

[a] Accuracy of molality within 0.05%.

Table VII. Coefficients of Equation $E_0 = a_0 + b_0T + c_0T^2$. $X$ = Weight % of 2-Propanol

| $X$ | $a_0 \times 10^2$ | $b_0 \times 10^3$ | $c_0 \times 10^6$ | S.D. |
|---|---|---|---|---|
| 8.03 | 89.432 | −3.9209 | 5.3911 | 0.0006 |
| 20.76 | −18.579 | 3.2461 | −6.6004 | 0.0001 |
| 44.04 | −3.9110 | 2.3252 | −5.3588 | 0.0003 |
| 70.28 | 38.060 | −0.3567 | −1.6289 | 0.0003 |
| 87.71 | −5.9269 | 2.8540 | −8.0913 | 0.0000 |

The values of the primary medium effect of 2-propanol–water mixed solvents upon hydrochloric acid are given in Table IV. An examination shows that the addition of small amounts of organic solvent (2-propanol) does not appreciably change the behavior of the medium upon the ions at infinite dilution. However, the medium has a greater effect upon the ions as the concentration of the organic solvent is slowly increased.

The values of the secondary medium effect presented in Table V seem to be normal and follow the general pattern of various mixed-solvent systems (*9, 14*).

The relative partial molal heat content, $\bar{L}_2$, and the relative partial molal heat capacities, $\bar{J}_2$, were calculated with the aid of the computer, using Equations 7 and 10 with

Table VIII. Relative Partial Molal Heat Content ($\overline{L}_2$) and Relative Partial Molal Heat Capacity ($\overline{J}_2$) of Hydrochloric Acid

| $m$/Mole Kg$^{-1}$ [a] | θ | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 0° C | | 15° C | | 25° C | | 35° C | |
| | $\overline{L}_2$ [b] | $\overline{J}_2$ | $\overline{L}_2$ | $\overline{J}_2$ | $\overline{L}_2$ | $\overline{J}_2$ | $\overline{L}_2$ | $\overline{J}_2$ |
| $X$ = 20.76 Weight % 2-Propanol | | | | | | | | |
| 0.01 | 2171 | 26 | 2583 | 28 | 2969 | 29 | 3165 | 30 |
| 0.005 | 2022 | 14 | 2249 | 15 | 2407 | 16 | 2570 | 16 |
| $X$ = 87.71 Weight % 2-Propanol | | | | | | | | |
| 0.1 | 5956 | 95 | 7424 | 100 | 8446 | 104 | 9504 | 107 |
| 0.02 | 3268 | 60 | 4196 | 63 | 4843 | 65 | 5511 | 67 |
| 0.01 | 2286 | 48 | 3040 | 51 | 3565 | 53 | 4108 | 55 |
| 0.002 | 1042 | 22 | 1392 | 23 | 1636 | 24 | 1889 | 25 |

Cal = 4.184 $J$

[a] Accuracy of molality within 0.05%. [b] $\overline{L}_2$, $\overline{J}_2$, cal mole$^{-1}$.

the appropriate coefficients presented in Tables VI and VII. The values of $\overline{L}_2$ and $\overline{J}_2$ for $X$ = 20.76 and 87.71 are given in Table VIII. Determination of $\overline{L}_2$ and $\overline{J}_2$ depends on the accuracy with which the temperature coefficient of the electromotive force can be determined and is very sensitive to experimental errors. High accuracy cannot be expected for the determination of $\overline{J}_2$, because the computation of $\overline{J}_2$ involves second-order differential coefficients of the original e.m.f. data, particularly when the concentration of organic solvent (2-propanol) is high. The data obtained from calorimetric measurements are better than those derived from electromotive force measurement. The limits of error for $\overline{L}_2$ and $\overline{J}_2$ are ±30 and ±10 cal, respectively.

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# Enthalpy of Formation of Bromotrinitromethane

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**The energy of reaction of liquid bromotrinitromethane with diethyl phthalate as a fuel was determined in a rotating bomb calorimeter. The standard enthalpy of formation of bromotrinitromethane was calculated to be +3.22 ± 0.24 kcal per mole (estimated standard deviation of the mean) at 298.2° K. The effect of temperature on density and vapor pressure of the compound was determined at a given temperature range.**

Enthalpies of formation of highly oxygenated compounds, such as bromotrinitromethane (BNF), are often determined by heat of solution techniques. This method usually requires the determination of a considerable amount of auxiliary data, thereby introducing additional experimental errors. Also, such additional data are usually applicable only for the particular compound under investigation. It is possible, but difficult, to determine enthalpies of formation by the usual calorimetric methods. The primary difficulty is the required tedious qualitative and quantitative analysis of the combustion products.

A calorimetric method developed at the Naval Ordnance Station *(10)* can be used to determine the enthalpy of formation of highly oxygenated compounds with known combustion products and standard analytical procedures. A solution of BNF (an oxidizer) and diethyl phthalate (a fuel) burns in a bomb under oxygen to form only carbon dioxide, nitrogen gas, and hydrogen bromide solution as

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