Excess Thermodynamic Functions for Ternary Systems
II. Chloroform–Ethanol–*n*-Heptane at 50°C

Joseph P. Shatas, Jr.,[1] Michael M. Abbott,[2] and Hendrick C. Van Ness[2]
Chemical and Environmental Engineering Department, Rensselaer Polytechnic Institute, Troy, N.Y. 12181

Extensive heat-of-mixing data for the ternary system chloroform–ethanol–*n*-heptane at 50°C are reported. Data are also presented for the three constituent binary systems at both 30° and 50°C. A correlation of the data at 50°C, together with a similar correlation for the excess free energy presented earlier, allows calculation of H^E, G^E, and S^E.

The experimental work leading to the results presented here differed only in detail from that reported in Part I (*4*) of this series of papers. Heat-of-mixing data for the binary systems chloroform(1)–ethanol(2), chloroform(1)–*n*-heptane(3), and ethanol(2)–*n*-heptane(3) were taken both at 30° and at 50°C. Twelve runs constituting 190 data points were taken for ternary mixtures of chloroform(1)–ethanol(2)–*n*-heptane(3) at 50°C. The courses of these runs are shown in Figure 1. The chloroform was chromatoquality reagent supplied by Matheson Coleman & Bell; the reagent-quality ethanol came from U.S. Industrial Chemicals; the *n*-heptane was the pure grade of Phillips Petroleum Co. All were used as received with a minimum indicated purity of 99.8 mol %.

Results and Correlations

Experimental values of H^E for the three binary systems are given in Table I for 30° and in Table II for 50°C (both tables deposited with the ACS Microfilm Depository Service). For the chloroform(1)–ethanol(2) and chloroform(1)–*n*-heptane(3) systems, these data are well correlated by equations of the form:

$$\frac{H^E}{x_i x_j RT} = A_{ji}x_i + A_{ij}x_j - (\lambda_{ji}x_i + \lambda_{ij}x_j)x_i x_j + (\psi_{ji}x_i + \psi_{ij}x_j)x_i^2 x_j^2 \quad (1)$$

This is the same equation used to correlate all of the data for the binary systems of Part I (*4*). However, it could not be used for the ethanol(2)–*n*-heptane(3) system. Rather, the following equation was found suitable in this case:

$$\frac{H^E}{x_2 x_3 RT} = A_{32}x_2 + A_{23}x_3 - \frac{\alpha_{23}\alpha_{32}x_2 x_3}{\alpha_{23}x_2 + \alpha_{32}x_3 + (\eta_{23}x_2 + \eta_{32}x_3)x_2 x_3} \quad (2)$$

Equation 2 is an extension of an equation developed earlier (*2*) for correlation of G^E for alcohol–hydrocarbon systems and called the modified Margules equation. It works nearly as well for fitting H^E data, though requiring terms of higher order in x, as is invariably the case in comparisons between representations of G^E and H^E data. The parameters determined for Equations 1 and 2 are given in Tables III and IV.

Figures 2–4 display all of our data in comparison with their correlating expressions for the three binary systems as plots of $H^E/x_i x_j RT$ vs. x_i. A minor deficiency in Equation 2 becomes evident in Figure 4 for ethanol–*n*-heptane. The values of $H^E/x_2 x_3 RT$ for very dilute ethanol solutions fall below the curve. The hooks at the ends of curves drawn through the experimental points are not artifacts, as has been repeatedly demonstrated by careful measurements (*5*, *6*) on alcohol–hydrocarbon systems. The failure to represent it is not of practical concern, because the value of H^E itself is rapidly approaching zero. We believe the correlating expressions represented by Equations 1 and 2 with parameters listed in Tables III and IV represent the data to within their experimental precision.

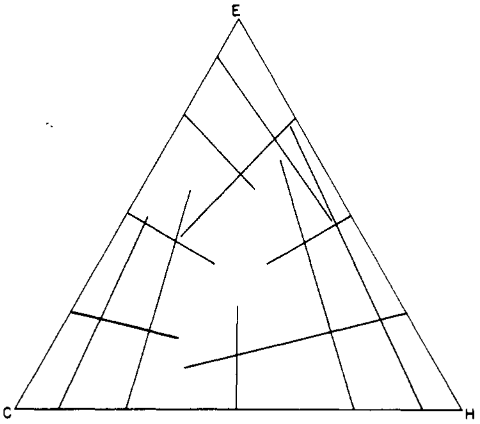

Figure 1. Lines showing compositions traversed during runs yielding heats of mixing for ternary mixtures

Table III. Correlating Parameters in Equation 1
Pairs of components are listed in order *i*, *j*

	Chloroform(1)–ethanol(2)		Chloroform(1)–*n*-heptane(3)	
	30°C	50°C	30°C	50°C
A_{ij}	−2.4322	−1.7611	1.1350	1.0198
A_{ji}	3.7860	3.8391	1.5413	1.3985
λ_{ij}	−0.4649	0.6995	0.1661	0.2336
λ_{ji}	15.8145	10.8501	0.4862	0.2999
ψ_{ij}	1.2813	6.2483	0.0	0.0
ψ_{ji}	33.2820	19.6898	0.0	0.0
σ (J/mol)	4.6	3.1	0.6	0.8
Max dev (J/mol)	11.2	9.3	1.1	2.1

Table IV. Correlating Parameters in Equation 2 for Ethanol(2)–*n*-Heptane(3)

	30°C	50°C
A_{23}	10.6488	10.4231
A_{32}	1.2478	1.4681
α_{23}	591.2876	292.9876
α_{32}	11.0298	10.4095
η_{23}	151.9309	84.9532
η_{32}	90.0913	41.9295
σ (J/mol)	1.9	2.9
Max dev (J/mol)	6.0	7.6

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[1] Present address, Knolls Atomic Power Laboratory, Schenectady, N.Y.
[2] To whom correspondence should be addressed.

Our results for the chloroform–ethanol system are fully consistent with those of Hirobe (*3*), and those for ethanol–*n*-heptane are in exact agreement with earlier values from this laboratory (*7*).

The 190 experimental values of H^E_{123} for the ternary system chloroform(1)-ethanol(2)-*n*-heptane(3) at 50°C are given in Table V (deposited with the ACS Microfilm Depository Service). The results are adequately correlated by the equations:

$$H^E_{123} = H^E_{12} + H^E_{13} + H^E_{23} + x_1x_2x_3\Delta_{123} \quad (3)$$

where

$$\Delta_{123}/RT = C_0 - C_1x_1 - C_2x_2 - C_3x_1^2 - C_4x_2^2 - C_5x_1x_2 - C_6x_1^3 - C_7x_2^3 - C_8x_1^2x_2 - C_9x_1x_2^2 \quad (4)$$

The various terms have the same significance as in the corresponding equations of Part I (*4*), and we reiterate the reservations with respect to the form of these equations as was expressed there.

The best-fit parameters, C_0 through C_9, for Equation 4 are listed in Table VI and provide a standard deviation between calculated and experimental values of H^E_{123} of about 10 J/mol

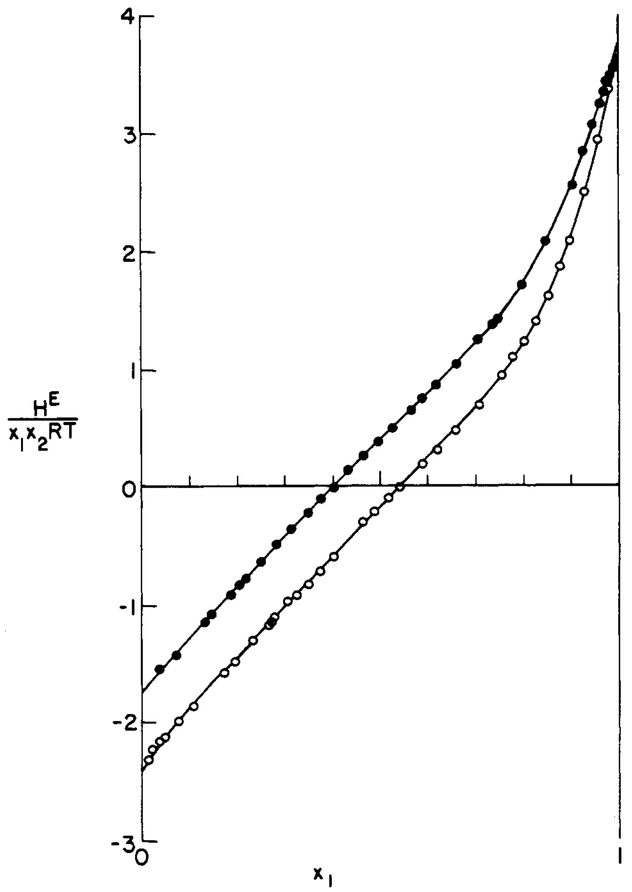

Figure 2. Correlation of H^E for binary system chloroform(1)-ethanol(2)

Points are experimental values; lines represent Equation 1 with appropriate parameters from Table III. ○, 30°C; ●, 50°C

Table VI. Correlating Parameters in Equation 4
Based on data for ternary mixtures of chloroform(1)–ethanol(2)–*n*-heptane(3)

C_0 = 13.6411 C_5 = −7.6855
C_1 = 4.8431 C_6 = 2.4544
C_2 = 43.9438 C_7 = 44.4992
C_3 = −3.8123 C_8 = −0.1245
C_4 = −72.6091 C_9 = −3.6770

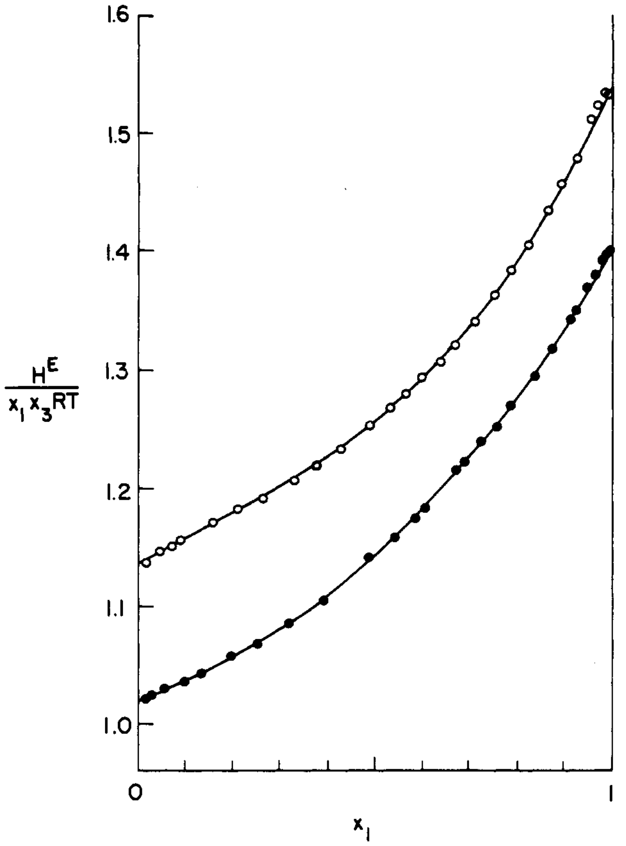

Figure 3. Correlation of H^E for binary system chloroform(1)-*n*-heptane(3)

Points are experimental values; lines represent Equation 1 with appropriate parameters from Table III. ○, 30°C; ●, 50°C

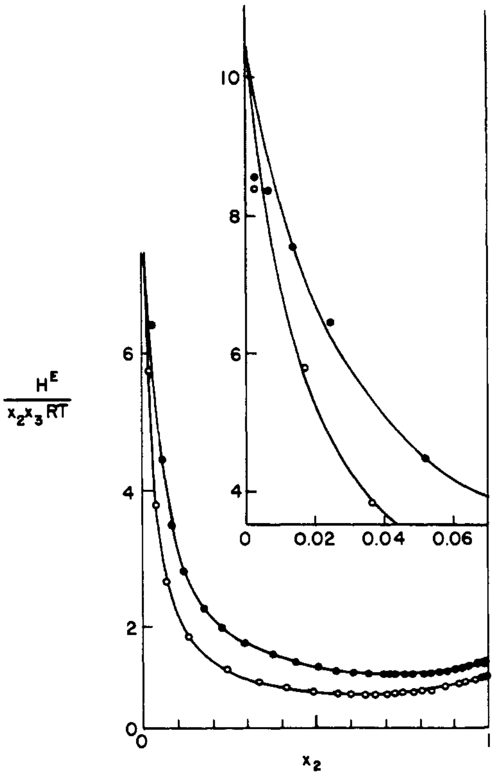

Figure 4. Correlation of H^E for binary system ethanol(2)-*n*-heptane(3)

Points are experimental values; lines represent Equation 2 with appropriate parameters from Table IV. ○, 30°C; ●, 50°C and a maximum deviation of about 30 J/mol. The quality of the fit is illustrated in Figure 5 by a plot of $[H^E_{123} - (1 - x_1)H^E_{23}\,(\text{initial})]/x_1(1 - x_1)RT$ vs. x_1 for the runs made by addition of pure chloroform to initial mixtures of ethanol and *n*-heptane.

The correlation presented here for H^E may be combined with an earlier correlation (*1*) for G^E for the same ternary system to provide values of S^E. As a result, it is possible to prepare triangular diagrams with mole fraction grids showing lines of constant values for the three functions, H^E_{123}, G^E_{123}, and TS^E_{123}; these diagrams appear as Figures 6–8.

Discussion

We repeat here a view expressed in Part I (*4*): Equations 3 and 4 are of a form not capable of representing our data for highly nonideal ternary mixtures to within their experimental precision. We present this correlation as an interim result, expressing the hope that our future attempts at significant improvement will meet with greater success than our substantial past efforts. Perhaps others will also respond to the challenge.

Nomenclature

A_{ij}, A_{ji} = parameters in Equations 1 and 2
$C_0, \ldots, C_9$ = parameters in Equation 4
G^E = excess Gibbs free energy
H^E = excess enthalpy or heat of mixing
R = universal gas constant
S^E = excess entropy
T = absolute temperature
x_i, x_j = mole fractions of components i and j

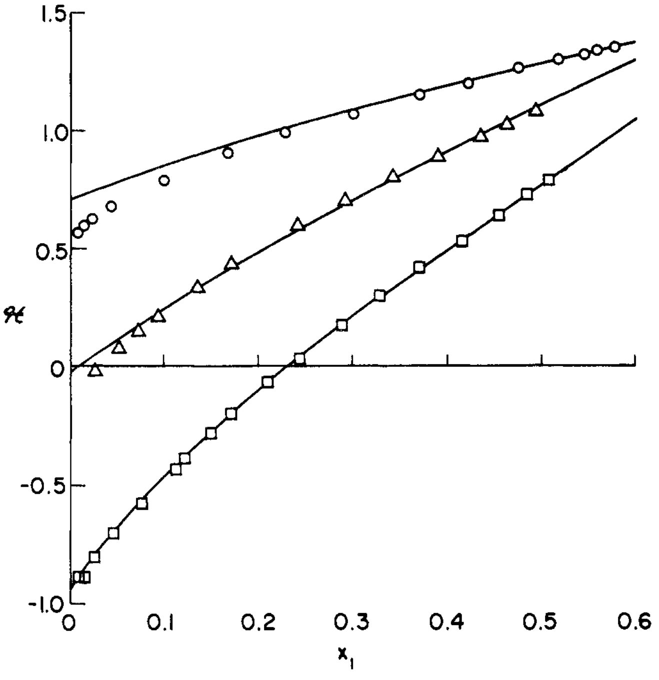

Figure 5. Correlation of results for ternary mixtures formed by addition of chloroform(1) to initial binary mixtures of ethanol(2)–*n*-heptane(3)

Function plotted is $\mathcal{H} = [H^E_{123} - (1 - x_1)H^E_{23}(\text{initial})]/x_1(1 - x_1)RT$. Points are experimental values, and lines represent correlation provided by Equations 3 and 4. ○, $x_2/x_3 = 0.335$; △, $x_2/x_3 = 0.994$; □, $x_2/x_3 = 3.00$

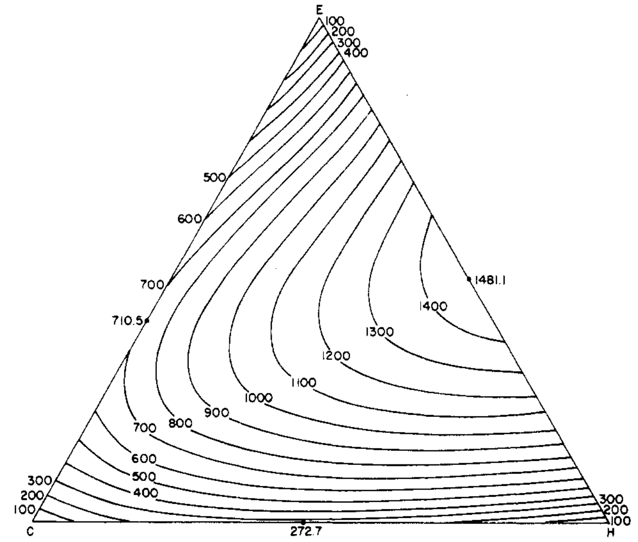

Figure 7. Lines of constant G^E in J/mol calculated from correlation for G^E given earlier (*1*)

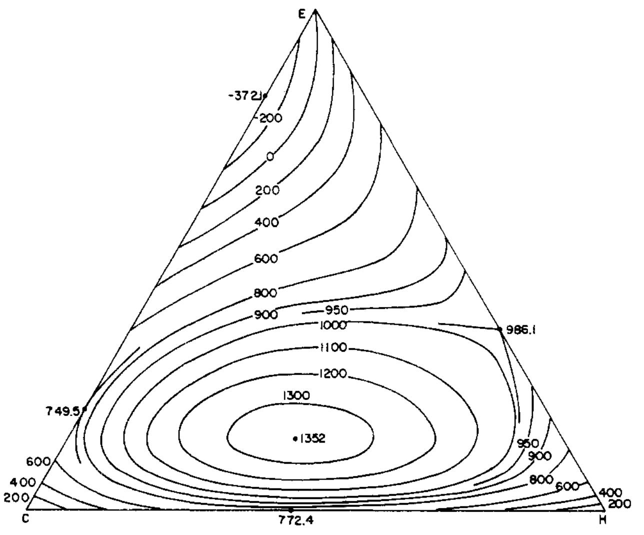

Figure 6. Lines of constant H^E in J/mol calculated from correlation of Equations 3 and 4 with parameters from Tables III, IV, and VI

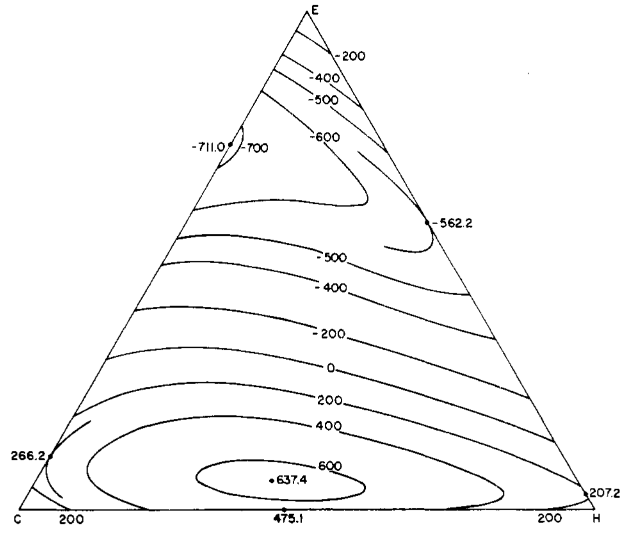

Figure 8. Lines of constant TS^E in J/mol calculated from correlations for H^E given here and for G^E given earlier (*1*)

Greek letters

Δ_{123} = function defined by Equation 4

$\alpha_{ij}, \alpha_{ji}, \eta_{ij}, \eta_{ji}$ = parameters in Equation 2

$\lambda_{ij}, \lambda_{ji}, \psi_{ij}, \psi_{ji}$ = parameters in Equation 1

σ = standard deviation

Literature Cited

(1) Abbott, M. M., Floess, J. K., Walsh, G. E., Van Ness, H. C., *AIChE J.*, **21**, 72 (1975).
(2) Abbott, M. M., Van Ness, H. C., *ibid.*, p 62.
(3) Hirobe, H., *J. Fac. Sci. Imp. Univ. Tokyo*, **1**, 155 (1925).
(4) Morris, J. W., Mulvey, P. J., Abbott, M. M., Van Ness, H. C., *J. Chem. Eng. Data*, 20 (4), 403 (1975).
(5) Savini, C. G., Winterhalter, D. R., Van Ness, H. C., *ibid.*, **10**, 168 (1965).
(6) Stokes, R. H., Burfit, C., *J. Chem. Thermodyn.*, **5**, 623 (1973).
(7) Van Ness, H. C., Soczek, C. A., Kochar, N. K., *J. Chem. Eng. Data*, **12**, 346 (1967).

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Supplementary Material Available. Tables I, II, and V will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JCED-75-406.

Conductances, Viscosities, and Densities of Solutions of Tetra-*n*-pentylammonium Thiocyanate in Nitrobenzene at 52°C

Philip H. Mogul
Great Neck South High School, Great Neck, N.Y. 11020

Peter H. Daum, Nehemiah Margalit, Jerome Levkov, William G. Rau, and Frederick R. Longo[1]
Chemistry Department, Drexel University, Philadelphia, Pa. 19104

The equivalent conductance of solutions composed of tetra-*n*-pentylammonium thiocyanate in nitrobenzene is measured from the fused salt region to 0.005410*N* at 52°C. Viscosity coefficients and densities are obtained over the range from the fused salt to pure solvent. The results show that the value of the $\Lambda\eta$-product at infinite dilution is approximately equal to the value for the fused salt. Contrary to our previous communication, the $\Lambda\eta$-product passes through a minimum as the concentration of the solution changes from *N* = 0 to *N* = 2.513 (fused salt).

In the early 1960's Kenausis, Evers, and Kraus (*2, 3*) (KEK) suggested that the product of the equivalent conductance and viscosity coefficient, $\Lambda\eta$, was a measure of ion dissociation in ultraconcentrated solutions of organic electrolytes. They proposed that the fused organic electrolytes were completely dissociated and that addition of solvent molecules caused aggregation by distorting the symmetrical fields about the ions. They used this hypothesis to explain the observation that $\Lambda\eta$ drops when solvent is added to the fused salt.

The ultraconcentrated region was defined roughly as the region between a solvent to electrolyte mole ratio (*N/n*) of 0.0–2.0. The ion fraction, F_i, was defined as $\Lambda\eta/(\Lambda\eta)_0$ where $(\Lambda\eta)_0$ is the value of the equivalent conductance-viscosity coefficient product for the fused salt. Kraus, Evers, and their students (*1-3, 8*) found that plots of $1 - F_i$ vs. *N/n* are linear up *N/n* ~ 2.0. These results were interpreted as support for two thermal mechanisms proposed to explain the conductance-viscosity behavior of concentrated and ultraconcentrated solutions.

In 1967 we communicated what we believed to be the anomalous behavior of the $\Lambda\eta$-product for the tetra-*n*-pentylammonium thiocyanate–nitrobenzene system at 52°C (*5*): We reported that the $\Lambda\eta$-product goes through a maximum in the ultraconcentrated region. Since that time we have convinced ourselves that we made an error in the calculation of the $\Lambda\eta$-product for this system, that it is quite normal, and, in fact, our observations may be interpreted to support the main KEK hypothesis, that the fused organic electrolyte is completely ionized.

Experimental

Preparation and purification of tetra-*n*-pentylammonium thiocyanate were accomplished by the methods of Longo et al. (*6*). The specific conductance obtained for this salt at 52.00° ± 0.01°C was 0.3102 mmho/cm, which agrees, within experimental error, with the value reported by Kenausis et al. (*2, 3*). Nitrobenzene (Matheson Coleman & Bell) was purified by a precedure described elsewhere (*7*). This method produced a solvent having a specific conductance of 1×10^{-10} ohm^{-1} cm^{-1}, which is good agreement with previously reported values (*6*).

Solution conductances were measured in two different cells. A conical cell having a cell constant 13.43 was utilized for the concentration range 2.417–0.005410*N*. A U-cell having a cell constant of 26.44 was used for the fused salt study and the ultraconcentrated solutions. This cell was designed to permit nitrogen gas mixing of the solution. All conductance measurements were made with a Wayne Kerr universal bridge Model No. B211. The cell constants were determined by the method of Lind et al. (*4*). Viscosities were determined with precalibrated Cannon-Ubbelohde viscometers with flow times measured by an electric timer to ±0.05 sec. Density values were obtained with a Christian-Becker specific gravity balance to ±0.0002 density units. All measurements were made in oil baths at 52°C with the temperature controlled to ±0.01°C. Temperature was monitored with a Beckmann dif-

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[1] To whom correspondence should be addressed.