

Standard Potential of Ag/AgCl Electrode in 25 and 50 wt % 2-Propanol-Water Solvents from 5 to 50 °C

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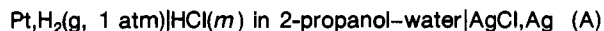
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Electromotive force measurements of cells of the type $\text{Pt, H}_2|\text{HCl}(m)$ in 2-propanol + $\text{H}_2\text{O}|\text{AgCl, Ag}$ at nine temperatures ranging from 5 to 45 °C were used to derive the standard emf of the cells in 25 and 50 wt % 2-propanol and the relative partial molal enthalpy of HCl. The molality of the acid ranged from 0.01 to 0.10 mol kg^{-1} . To obtain the standard emf it was necessary to use the extended terms of the Debye-Hückel theory. The standard emf varied with temperature (t , °C) according to the following equations: (25%) $E_m^\circ = 0.21383 - (3.945 \times 10^{-4})t - (5.24 \times 10^{-6})t^2$; (50%) $E_m^\circ = 0.19607 - (6.658 \times 10^{-4})t - (5.52 \times 10^{-6})t^2$.

Introduction

2-Propanol is a very useful solvent for organic compounds. In order to study the properties of electrolytes in this solvent and its mixtures with water, it is important to determine the standard potentials of electrodes in 2-propanol-water solvents. The silver-silver chloride electrode is of the highest importance in this respect, in view of its application to the determination of activity coefficients, equilibrium constants, and other related thermodynamic quantities in a variety of solvent media (1-6).

From early studies of the emf of the cell



Harned and Calmon (1) determined the standard potential of the silver-silver chloride electrode in a solvent mixture containing 10% by weight of 2-propanol and 90% water at 25 °C. This work was later extended by Moore and Felsing (2) to include solvents of the compositions 5, 10, and 20 wt %. Their work covered the temperature range 0-40 °C at intervals of 5 °C. At 25 °C, their value of E° (molality scale) differed from that of Harned and Calmon by only 0.2 mV. In both investigations, the standard potential was determined by an extrapolation to an ionic strength (I) of zero with the aid of the Debye-Hückel equation.

The most extensive study of cell A is that of Roy and Bothwell (7, 8), who made emf measurements at several different solvent compositions, 8.08, 20.76, 44.04, 70.28, and 87.71 wt % 2-propanol, and at temperatures of 0, 15, 25, and 35 °C. Standard potentials were obtained by a polynomial curve-fitting procedure which did not require a knowledge of the dielectric constants and densities of the solvent media or an estimate of the ion-size parameter.

In this investigation we have chosen to determine the standard potential in the useful mixtures composed of 25 and 50 wt % 2-propanol and have extended the temperature range to 45 and 50 °C, respectively.

Experimental Procedures

The 2-propanol was obtained commercially and purified by two fractional distillations. Doubly distilled hydrochloric acid was used to make stock solutions of the desired concentrations. The cell solutions were prepared by diluting the stock solutions with doubly distilled water and adding the calculated amounts

of 2-propanol by weight. The cell vessels were of all-glass construction of a design described earlier (9). The preparation of the hydrogen electrodes and the silver chloride-silver electrodes followed the instructions given by Bates (10). Hydrogen gas was purified by passage through a De-Oxo catalytic purifier. The AgCl/Ag electrodes were intercompared in a dilute solution of HCl and only those whose bias potentials were within 0.1 mV of the average of the set were used. Temperature measurements were made with a calibrated thermometer. Measurements of emf were made with the aid of a Fluke potentiometer, Model 8800A. The accuracy of the Fluke 8800A was checked on a regular basis using the procedure suggested by Bates and Macaskill (13). Other experimental details were essentially the same as described earlier (11).

We made initial measurements of the emf at 25 °C, after which the temperature of the water bath was lowered to 5 °C and raised gradually to 25 °C, waiting for equilibrium to be attained at each of the selected temperatures. The bath temperature was then raised, and the emf at 30 to 45 or 50 °C was obtained. At the conclusion of the run, the cells were brought back to 25 °C to test their stability. On the average, the initial and final values differed by 0.1 mV.

Results

The recorded values of the emf were corrected to a hydrogen partial pressure of 760 torr (101.325 kPa) in the usual way. The correction (ΔE) to be added is given by

$$\Delta E = \frac{RT}{2F} \ln \frac{760}{p_{\text{H}_2}} \quad (1)$$

were p_{H_2} , the partial pressure of hydrogen, is the barometric pressure less the vapor pressure of the solvent. Solvent vapor pressures were taken from the literature when available; otherwise they were estimated from those of the pure components, assuming ideal mixing. The corrected emf data are listed in Table I.

Apparent values, $E^{\circ'}$, of the standard emf E° were calculated by the equation

$$E^{\circ'} = E^\circ - 2k\beta m = E + 2k \log m - 2k \frac{Am^{1/2}}{1 + B\hat{a}m^{1/2}} \quad (2)$$

in which the extended Debye-Hückel expression has been substituted for the mean activity coefficient of HCl, and k is written for $(RT \ln 10)/F$. The "true" value of E° is the limit of $E^{\circ'}$ at $m = 0$. The Debye-Hückel constants A and B for the solvent mixtures were calculated by equations given elsewhere (10, p 248) with the aid of the solvent densities and dielectric constants. The ion-size parameter \hat{a} was chosen as 4.3 Å, the value characteristic of HCl in water at 25 °C (11) and in several mixed solvent media as well.

With these values of the parameters, $E^{\circ'}$ was essentially a linear function of the molality m , and the intercept E° was obtained by linear regression methods. The values of E° (molality scale) are summarized in Tables II and III, together with the dielectric constants (ϵ), vapor pressures (p), and densities (d) of the solvents and the Debye-Hückel constants A and B . The standard deviations, s , for regression from the straight

Table I. Electromotive Force of Cell Pt,H₂(g, 1 atm)|HCl(m) in 2-Propanol (X)-Water|AgCl,Ag

<i>m</i> _{HCl}	<i>E</i> , V									
	5 °C	10 °C	15 °C	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C
<i>X</i> = 25 wt % = 0.091 Mole Fraction										
0.091 34	0.341 13	0.341 87	0.341 93	0.342 16	0.341 19	0.339 52	0.338 29	0.337 11	0.335 32	
0.080 00	0.347 39	0.348 33	0.349 17	0.349 47	0.349 63	0.348 05	0.346 32	0.345 60	0.344 81	
0.071 46	0.352 02	0.352 99	0.353 52	0.353 66	0.353 48	0.352 15	0.351 22	0.349 88	0.348 63	
0.066 30	0.354 45	0.355 60	0.356 29	0.356 54	0.356 31	0.355 28	0.354 25	0.353 45	0.352 20	
0.058 23	0.361 82	0.362 90	0.363 56	0.363 77	0.363 58	0.363 61	0.362 92	0.362 14	0.360 56	
0.042 50	0.374 66	0.375 96	0.376 80	0.377 23	0.376 68	0.376 62	0.376 27	0.375 77	0.374 91	
0.034 79	0.383 53	0.385 01	0.386 00	0.386 53	0.385 93	0.385 84	0.385 52	0.385 46	0.384 61	
0.029 68	0.390 62	0.391 96	0.393 04	0.393 60	0.393 11	0.394 26	0.394 30	0.393 56	0.393 31	
0.027 77	0.392 92	0.394 57	0.395 71	0.396 36	0.396 78	0.396 90	0.396 69	0.395 45	0.394 61	
<i>X</i> = 50 wt % = 0.231 Mole Fraction										
0.019 467	0.395 27	0.395 39	0.395 55	0.395 18	0.393 63	0.393 22	0.392 39	0.390 74	0.389 19	0.386 83
0.047 05	0.358 56	0.358 13	0.357 34	0.356 25	0.354 69	0.353 18	0.351 50	0.349 42	0.347 08	0.344 38
0.097 19						0.321 90	0.319 63	0.317 14	0.314 37	0.311 34
0.108 98	0.324 88	0.323 86	0.322 69	0.321 12	0.319 07	0.316 96	0.314 60	0.312 03	0.309 29	0.306 32
0.121 56	0.319 47	0.318 38	0.316 99	0.315 55	0.314 00	0.311 88	0.309 52	0.306 98	0.304 26	0.301 29
0.134 70	0.315 80	0.314 72	0.313 22	0.311 36	0.309 33	0.307 22	0.304 66	0.301 99	0.299 17	0.296 12

Table II. Properties of the Solvents, Constants of Eq 2, and Values of the Standard Emf of Cell A in 25 wt % 2-Propanol-Water

<i>t</i> , °C	<i>ε</i>	<i>p</i> , torr	<i>d</i> , g cm ⁻³	<i>A</i>	<i>B</i>	<i>E</i> ^o , V	<i>s</i> (<i>E</i> ^o), mV
5	68.23	6.9	0.968 86	0.6871	0.3593	0.2118	0.5
10	67.14	9.6	0.965 86	0.6843	0.3585	0.2100	0.5
15	65.16	13.3	0.963 37	0.6962	0.3602	0.2077	0.6
20	63.83	18.2	0.960 71	0.6989	0.3603	0.2048	0.6
25	61.70	24.6	0.957 51	0.7157	0.3628	0.2009	0.8
30	60.26	33.0	0.954 97	0.7223	0.3636	0.1988	0.9
35	59.02	43.8	0.951 99	0.7260	0.3638	0.1957	0.9
40	57.69	57.6	0.949 21	0.7323	0.3645	0.1915	1.0
45	55.72	77.1	0.945 60	0.7519	0.3673	0.1873	1.1

Table III. Properties of the Solvent, Constants of Eq 2, and Values of the Standard Emf of Cell A in 50 wt % 2-Propanol-Water

<i>t</i> , °C	<i>ε</i>	<i>p</i> , torr	<i>d</i> , g cm ⁻³	<i>A</i>	<i>B</i>	<i>E</i> ^o , V	<i>s</i> (<i>E</i> ^o), mV
5	47.42	7.5	0.917 52	1.1540	0.4194	0.1926	0.5
10	46.17	10.5	0.912 80	1.1676	0.4204	0.1888	0.4
15	44.89	14.5	0.907 52	1.1818	0.4212	0.1850	0.5
20	43.68	19.8	0.904 86	1.1981	0.4228	0.1808	0.4
25	42.50	26.8	0.902 23	1.2153	0.4244	0.1754	0.3
30	41.35	36.0	0.899 12	1.2330	0.4259	0.1710	0.3
35	40.23	47.7	0.896 56	1.2519	0.4277	0.1663	0.3
40	39.16	62.8	0.894 89	1.2713	0.4296	0.1607	0.3
45	38.9	81.9	0.887 85	1.2890	0.4305	0.1551	0.3
50	37.03	106.0	0.880 78	1.3085	0.4315	0.1488	0.3

lines used for extrapolation are given in the last column. Densities of the solvent mixtures were taken from the literature, and the dielectric constants were furnished by Dr. S. D. Klein (12).

Discussion

The values of *E*_{*m*}^o (molality scale) as a function of temperature (*t*, °C) are given by the quadratic equations

25 wt %

$$E_m^o = 0.21383 - (3.945 \times 10^{-4})t - (5.24 \times 10^{-6})t^2$$

$$s = 0.5 \text{ mV} \quad (3)$$

50 wt %

$$E_m^o = 0.19607 - (6.658 \times 10^{-4})t - (5.52 \times 10^{-6})t^2$$

$$s = 0.3 \text{ mV} \quad (4)$$

where *s* stands for the standard deviation of the fit of the polynomial. The mean activity coefficients γ_{\pm} of HCl in the two 2-propanol-water mixtures can be readily calculated from the

Table IV. Comparison of Values of *E*_{*m*}^o at 25 °C with Literature Values

[2-propanol], wt %	<i>E</i> _{<i>m</i>} ^o , V			
	present work	MF ^a	RB ^b	RB ^c
10		0.2138	0.2040	
		0.2136 ^d		
20		0.2064	0.1952	0.2063
25	0.2009		0.1909	0.2009
50	0.1754		0.1632	0.1739

^a Moore and Felsing (2). ^b Roy and Bothwell (7, 8). ^c Roy and Bothwell, recalculated. ^d Harned and Calmon (1).

emf given in Table I and the *E*^o values given in Tables II and III by the equation

$$-\log \gamma_{\pm} = \frac{E - E^o}{2k} + \log m \quad (5)$$

Roy and Bothwell (7, 8) have determined *E*_{*m*}^o (molality scale) at five solvent compositions from 8.08 to 87.7 wt %. We have converted their values at 25 °C to the mole fraction scale (*E*_{*N*}^o)

Table V. Electromotive Force of Cell Pt,H₂(g, 1 atm)|HCl(m) in 50 wt % 2-Propanol-Water|AgCl,Ag^a

<i>m</i> _{HCl}	<i>E</i> , V									
	5 °C	10 °C	15 °C	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C
0.019 467	0.391 15 (761.0)	0.395 22 (761.2)	0.395 31 (761.4)	0.394 86 (761.0)	0.393 17 (760.2)	0.392 57 (759.3)	0.391 48 (759.4)	0.389 52 (759.8)	0.387 62 (760.6)	0.384 75 (758.8)
0.047 051	0.358 38 (758.5)	0.357 91 (759.0)	0.357 07 (760.0)	0.355 77 (758.2)	0.354 20 (759.0)	0.352 51 (756.0)	0.350 58 (755.4)	0.348 19 (755.2)	0.355 46 (757.6)	0.342 24 (757.7)
0.097 195						0.321 26 (760.2)	0.318 81 (761.4)	0.316 03 (761.6)	0.312 86 (762.0)	0.302 99 (760.2)
0.108 98	0.324 75 (762.0)	0.323 69 (762.2)	0.322 45 (762.0)	0.320 78 (761.0)	0.318 62 (761.4)	0.316 32 (760.2)	0.313 78 (761.4)	0.310 92 (761.6)	0.307 78 (762.0)	0.304 27 (760.2)
0.121 56	0.319 34 (762.0)	0.318 21 (762.2)	0.316 75 (762.0)	0.315 21 (761.0)	0.313 55 (761.4)	0.311 24 (760.2)	0.308 70 (761.4)	0.305 87 (761.6)	0.302 75 (762.0)	0.299 24 (762.2)
0.134 70	0.315 67 (762.0)	0.314 54 (762.2)	0.312 98 (762.0)	0.311 02 (761.0)	0.308 88 (761.4)	0.306 61 (760.2)	0.303 84 (761.4)	0.300 88 (761.6)	0.297 66 (762.0)	0.294 07 (760.2)

^a Primary measurements; barometric pressure in parentheses.

Table VI. Electromotive Force of Cell Pt,H₂(g, 1 atm)|HCl(m) in 25 wt % 2-Propanol-Water|AgCl,Ag^a

<i>m</i> _{HCl}	<i>E</i> , V									
	5 °C	10 °C	15 °C	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	
0.091 340	0.341 00 (761.5)	0.341 70 (762.2)	0.342 05 (762.2)	0.341 85 (762.6)	0.340 77 (763.0)	0.338 92 (761.6)	0.337 48 (761.6)	0.336 04 (762.4)	0.333 89 (762.8)	
0.080 000	0.347 29 (763.4)	0.348 17 (763.0)	0.348 97 (763.9)	0.349 18 (763.9)	0.348 91 (663.7)	0.347 48 (763.6)	0.345 53 (763.0)	0.344 53 (762.4)	0.343 38 (762.9)	
0.071 460	0.351 92 (763.4)	0.352 83 (763.0)	0.353 36 (763.9)	0.353 37 (763.9)	0.352 76 (764.6)	0.351 58 (763.6)	0.350 43 (763.0)	0.348 81 (762.4)	0.347 20 (762.9)	
0.066 304	0.354 42 (762.0)	0.355 43 (761.9)	0.356 06 (762.1)	0.356 23 (762.7)	0.355 89 (763.0)	0.354 68 (761.9)	0.353 43 (761.4)	0.352 35 (760.9)	0.350 73 (760.7)	
0.058 233	0.361 69 (762.0)	0.362 73 (761.9)	0.363 33 (762.1)	0.363 46 (762.7)	0.363 16 (763.0)	0.363 01 (761.9)	0.362 10 (761.4)	0.361 04 (760.9)	0.359 15 (763.7)	
0.042 500	0.374 56 (763.4)	0.375 80 (763.0)	0.376 60 (763.9)	0.376 94 (763.9)	0.375 97 (746.6)	0.376 05 (763.6)	0.375 48 (763.0)	0.374 70 (762.4)	0.373 48 (762.0)	
0.034 790	0.383 43 (763.4)	0.384 85 (763.0)	0.385 80 (763.9)	0.386 24 (763.9)	0.385 22 (746.6)	0.385 27 (763.6)	0.384 73 (763.0)	0.384 39 (762.4)	0.383 18 (762.9)	
0.029 680	0.390 53 (764.2)	0.391 83 (764.7)	0.392 85 (764.6)	0.393 32 (764.7)	0.392 68 (762.4)	0.393 69 (763.6)	0.393 54 (764.4)	0.392 52 (764.1)	0.391 90 (763.7)	
0.027 700	0.392 77 (761.5)	0.394 40 (762.2)	0.395 48 (762.2)	0.396 05 (762.6)	0.396 36 (763.0)	0.396 30 (761.6)	0.395 88 (761.6)	0.394 38 (762.4)	0.393 18 (762.8)	

^a Primary measurements; barometric pressure in parentheses.

and have interpolated at 20, 25, and 50 wt % graphically on a plot of E_N° vs. mole fraction of 2-propanol. The outlying point at 44.4 wt % was ignored. The results, converted to E_m° by the relationship

$$E_m^\circ = E_N^\circ - 2k \log 0.001M_s \quad (6)$$

where M_s is the mean molecular weight of the solvent mixture, are given in Table IV for comparison with the present results and with the earlier data for 10 and 20 wt % 2-propanol (1, 2).

It is evident that the standard emf values of Roy and Bothwell are from 9 to 12 mV lower than those of this study and the earlier work of Harned and Calmon (1) and Moore and Felsing (2). This difference is much too large to be attributed to experimental error. Its cause has been sought in the method of data treatment. Roy and Bothwell determined E_m° as the intercept at $m^{1/2} = 0$ of plots of $E + 2k \log m$ as a function of $m^{1/2}$, using curve-fitting procedures. No estimates of activity coefficients (as in the last term of eq 1) were made, and thus a knowledge of the dielectric constants and densities of the solvents was unnecessary. This procedure accords undue weight to the solutions most dilute in HCl, where the experimental errors are greatest.

Examination of their data suggests that the emf for the two solutions of molality less than 0.005 mol kg⁻¹ may be low. A recalculation of the data for 20.76 wt % 2-propanol, using eq 1, for example, yields $E_m^\circ = 0.2050$ V, with a standard deviation of regression (*s*) of 1.7 mV. When the two lowest points are omitted, however, E_m° is found to be 0.2063 V with *s* = 0.3 mV. The latter value is in excellent agreement with 0.2064

V found by Moore and Felsing (2) for the 20 wt % mixture. The recalculation was therefore extended to the data of Roy and Bothwell at 44.04, 70.28, and 87.71 wt % 2-propanol, omitting as before the two lowest molalities of HCl. The recalculated value at 44.04 wt % was now found to be consistent with those at the other solvent compositions, and graphical interpolation on a plot of E_N° vs. mole fraction of 2-propanol yielded a value of E_m° at 25 wt % in agreement with that found in the present study. The results of the recalculation are given in the last column of Table IV.

Primary measurements, e.g., the immediately measured emf values and barometric pressure in parentheses, are reported in Tables V and VI. These values should allow one to recalculate the results using any correction procedure.

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Registry No. Ag, 7440-22-4; AgCl, 7783-90-6; HCl, 7647-01-0; 2-propanol, 67-63-0.

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Viscosities and Activation Energies of Viscous Flow of the Binary Mixtures of *n*-Hexane with Toluene, Chlorobenzene, and 1-Hexanol

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Viscosities of three binaries, viz., *n*-hexane-toluene, *n*-hexane-chlorobenzene, and *n*-hexane-1-hexanol, have been determined at 30, 40, 50, and 60 °C over the complete composition range. Experimental viscosities are compared with values calculated by using equations based on the concept of significant liquid structures as well as McAllister type three-body interactions. Energies of activation for viscous flow have been obtained and their variations with composition have been discussed.

Introduction

As part of a program (1-3) to collect and correlate viscosity data of binary liquid mixtures with varying nonideality, we have determined the viscosities and activation energies of the binary mixtures *n*-hexane (1)-toluene (2), *n*-hexane (1)-chlorobenzene (2), and *n*-hexane (1)-1-hexanol (2) in the temperature range 30-60 °C and tested the predictive abilities of viscosity equations based on the concept of significant liquid structures (SLS) (4) as well as McAllister type three-body interactions (5).

Experimental Section

All the organic chemicals, viz, *n*-hexane, toluene, chlorobenzene, and 1-hexanol, used in the present study were of BDH origin. These were purified (6) by fractional distillation and drying and the experimental values of their densities, refractive indices, and viscosities checked with the corresponding literature values (7), within allowed limits. The binary liquid mixtures were prepared by weighing the individual components and the viscosities were measured with the help of a thoroughly cleaned, dried, and calibrated Ostwald viscometer following standard experimental procedure described elsewhere (8a). Due care was taken to ascertain that limbs of the viscometer coincided with the vertical within 0.5°. The time of flow was determined cautiously several times and the standard deviations were found well within 0.1%. Further, the densities required were measured by the standard method (8b) using a specific gravity bottle and the same were used along with the measured absolute viscosity data to obtain the corresponding kinematic viscosities. In each case, the viscosity and density measurements were carried out in a Toshniwal GL-15 precision thermostat limiting the temperature fluctuations to ±0.1 °C.

The uncertainty in viscosity measurements entered in the fourth decimal place for the binaries rich in *n*-hexane, toluene, and chlorobenzene and in the third decimal place for the binaries rich in 1-hexanol. As regards densities, the repeat

measurements differed by a few units only in the fourth decimal place in each case.

Results and Discussion

The experimental viscosity-composition-temperature data for the title binaries are recorded in Tables I-III. The mixture kinematic viscosities ν_m were used to test the following equation (5) based on McAllister type three-body interactions:

$$\ln \nu_m = X_1^3 \ln \nu_1 + X_2^3 \ln \nu_2 + 3X_1^2 X_2 \ln \nu_{12} + 3X_1 X_2^2 \ln \nu_{21} - \ln [X_1 + X_2 M_2 / M_1] + 3X_1^2 X_2 \ln \left[\frac{2 + M_2 / M_1}{3} \right] + 3X_1 X_2^2 \ln \left[\frac{1 + 2M_2 / M_1}{3} \right] + X_2^3 \ln M_2 / M_1 \quad (1)$$

where ν is the kinematic viscosity in centistokes, M is the molecular weight, X is the mole fraction, and the subscripts m , 1, and 2 represent the mixture and components 1 and 2, respectively, while ν_{12} and ν_{21} are mixture interaction parameters to be determined from experimental data and are given in Table IV.

Again the absolute viscosity data were used to test the following equation (4) based on the SLS concept:

$$\eta_m = \frac{Nh}{r_m} \frac{6}{2^{1/2}} \frac{1}{(1 - e^{-\Theta_1/T})^{X_1}} \frac{1}{(1 - e^{-\Theta_2/T})^{X_2}} \frac{1}{(V_m - V_{sm})} \times \exp \frac{a_m E_{sm} V_{sm}}{RT(V_m - V_{sm})} + \frac{V_m - V_{sm}}{V_m} \left[\frac{2}{3d_1^2} \left(\frac{m_1 kT}{\pi^3} \right)^{1/2} X_1 + \frac{2}{3d_2^2} \left(\frac{m_2 kT}{\pi^3} \right)^{1/2} X_2 \right] \quad (2)$$

where η is the absolute viscosity, V is the molar volume, V_s is the solidlike volume in V , Θ is the Einstein characteristic temperature, E_s is the energy of sublimation, m is the mass of a single molecule with diameter d in the gaseous state, and a is determined by another parameter n whereas r is equal to the product of the number of nearest neighbors Z and the transmission coefficient κ . Since it is difficult to determine the value of Z a priori and evaluate κ theoretically, r is treated as a disposable parameter and is usually fixed by forcing agreement between the experimental and calculated viscosities at each temperature. The values of V , V_s , and M for the binary components were taken from an earlier work (7) and those of E_s , Θ , a , n , d , and r were evaluated by following the procedure of Singh and Sinha (7) and listed in Table V. The mixture

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