Viscosity and Density for Binary Mixtures of Carbon Tetrachloride + Chloroform, Carbon Tetrachloride + Dichloromethane, and Chloroform + Dichloromethane and One Ternary Mixture of Chloroform + 1:1 (Carbon Tetrachloride + Dichloromethane) at 303.15 K

Hai-Lang Zhang*

Department of Chemistry, Fuzhou University, Fuzhou City, 350002 Fujian Province, P. R. China

Viscosity and density have been measured for three binary mixtures of chlorinated methanes, that is, carbon tetrachloride + chloroform, carbon tetrachloride + dichloromethane, and chloroform + dichloromethane, and for one ternary mixture of 1:1 mole ratio (carbon tetrachloride + dichloromethane) + chloroform at 303.15 K. Molar excess volumes V^E and viscosity deviations were obtained for these mixtures. Molecular interactions have been interpreted from the results. There are very weak specific interactions between CCl_4 and CH_2Cl_2 or between CCl_4 and $CHCl_3$. There are relatively stronger specific interactions between $CHCl_3$ and CH_2Cl_2. The interactions between different chlorinated methanes decrease in the order CH_2Cl_2 - - - $CHCl_3$ > CCl_4 - - - CH_2Cl_2 > CCl_4 - - - $CHCl_3$. The interactions are considered to be caused mainly by the differences in polarity, size, and shape between different component molecules.

1. Introduction

As fundamental and important properties of liquids, viscosity and volume could also provide a lot of information on the structures and molecular interactions of liquid mixtures. Viscosity and volume are different types of properties of one liquid, and there is a certain relationship between them. So by measuring and studying them together, relatively more realistic and comprehensive information could be expected to be gained. The relationship between them could also be studied.

Although there are many works on either volume measurements or viscosity measurements of liquid mixtures, there are much fewer investigations on them together. So studies on the relationship between them are scarce. Much more attention has been paid to this aspect by me.[1,2] On this aspect the achievements were first made by Singh[3] and Singh et al.[4]

Relatively, viscometric properties could provide more and deeper information on molecular interactions. For example, the Grunberg−Nissan equation[5] may quantitively describe molecular interactions in one binary liquid mixture. From this equation, one parameter, called the interaction parameter by Fort and Moore,[6] can be obtained. This way, the molecular interactions could be known better.[7,8] Katti and Chandhri[9] also reached an expression to quantitively describe molecular interactions in one binary liquid mixture.

In this paper special attention has been paid to chlorinated methanes, that is, dichloromethane, chloroform, and carbon tetrachloride. They are not only important and excellent widely used solvents but also structurally related, with being typical of only one carbon atom. So more systematical and detailed information could be expected by studying their mixtures. Here three binary mixtures (carbon tetrachloride + chloroform, carbon tetrachloride + dichloromethane, and chloroform + dichloromethane) are concerned. Also one ternary mixture [1:1 (carbon tetrachloride + dichloromethane) + chloroform] has been prepared. In my previous work,[2] the 1:1 mole ratio (carbon tetrachloride + dichloromethane) was successfully defined as pseudochloroform. It is expected to be investigated furthermore in this paper. In this work viscosity and molar excess volume were measured at 303.15 K for these binary mixtures and one ternary mixture.

There are no literature viscosity data available for all these mixtures. There are also no excess molar volume data at 303.15 K for all these mixtures in the literature. For carbon tetrachloride + chloroform, there are literature V^E values at 298.15 K[10] and at temperatures higher than 308.15 K.[11] For carbon tetrachloride + dichloromethane, there are literature V^E values[12,13] at (298.15, 308.15, and 318.15) K. For chloroform + dichloromethane, V^E values only at 298.15 K could be found in the literature.[12]

2. Experimental Section

Carbon tetrachloride (A.R.) was dried over anhydrous calcium chloride and distilled over phosphorus pentoxide. Chloroform (A.R.) was shaken several times with about half of its volume of distilled water, dried over anhydrous calcium chloride, and then fractionally distilled. Dichloromethane (A.R.) was fractionally distilled over calcium oxide, and the middle colorless fractions were collected. The purities of the components can be further ascertained by measuring their densities and viscosities at 303.15 K and comparing them with available literature values. The comparison is made in Table 1. It can be found from Table 1 that the results are satisfying. The density and viscosity for the 1:1 (carbon tetrachloride + dichloromethane) prepared in this work are also listed in Table 1.

Binary or ternary mixtures were made by mass with a weighing precision of $\pm 5 \times 10^{-5}$ g in mixing bottles similar to those used by Takenake et al.[17] The bottles are evapora-

---

* E-mail: zhl8868@hotmail.com.

10.1021/je020067x CCC: $25.00

Table 1. Densities ρ and Viscosities η of Pure Component Liquids and 1:1 ($CCl_4 + CH_2Cl_2$) at 303.15 K

	ρ/g·cm^{-3}		η/mPa·s	
	exp	lit.	exp	lit.
carbon tetrachloride	1.5750	1.5749;[14] 1.5748[15]	0.8403	0.845;[15] 0.847[16]
chloroform	1.4705	1.4706[15]	0.5118	0.514;[15] 0.517[16]
dichloromethane	1.3076	1.3077[15]	0.3929	0.393;[15] 0.395[16]
1:1 ($CCl_4 + CH_2Cl_2$)[a]	1.4629		0.5376	

[a] The actual mole fraction of CCl_4 is 0.5002.

Table 2. Experimental Values of Density ρ, Viscosity η, Viscosity Deviation $\Delta\eta$, and Excess Molar Volume V^E for Mixtures at 303.15 K

x	ρ/g·cm^{-3}	η/mPa·s	$\Delta\eta$/mPa·s	V^E/cm^3·mol^{-1}
$(x)CCl_4 + (1 - x)CH_2Cl_2$				
0.0375	1.3215	0.4008	−0.0089	0.045
0.0622	1.3304	0.4061	−0.0146	0.073
0.0791	1.3364	0.4097	−0.0186	0.090
0.0889	1.3399	0.4120	−0.0207	0.097
0.1254	1.3524	0.4210	−0.0280	0.134
0.2047	1.3784	0.4410	−0.0435	0.198
0.2305	1.3865	0.4479	−0.0481	0.217
0.2970	1.4067	0.4669	−0.0589	0.254
0.3695	1.4277	0.4897	−0.0685	0.278
0.4985	1.4625	0.5369	−0.0790	0.295
0.4986	1.4625	0.5374	−0.0786	0.297
0.4997	1.4628	0.5375	−0.0790	0.296
0.5631	1.4789	0.5640	−0.0808	0.287
0.6090	1.4901	0.5853	−0.0801	0.279
0.6845	1.5080	0.6223	−0.0768	0.247
0.8006	1.5339	0.6894	−0.0617	0.184
0.8032	1.5345	0.6915	−0.0608	0.180
0.8652	1.5477	0.7331	−0.0469	0.132
0.9279	1.5607	0.7792	−0.0288	0.071
0.9677	1.5686	0.8116	−0.0142	0.037
$(x)CCl_4 + (1 - x)CHCl_3$				
0.0591	1.4772	0.5216	−0.0096	0.036
0.0750	1.4790	0.5248	−0.0116	0.044
0.1297	1.4851	0.5343	−0.0201	0.072
0.2236	1.4953	0.5538	−0.0315	0.119
0.2777	1.5012	0.5658	−0.0372	0.134
0.3416	1.5081	0.5811	−0.0429	0.147
0.4340	1.5179	0.6041	−0.0503	0.160
0.4886	1.5236	0.6201	−0.0522	0.163
0.5736	1.5325	0.6486	−0.0516	0.153
0.6646	1.5418	0.6807	−0.0494	0.138
0.7747	1.5529	0.7256	−0.0407	0.106
0.8186	1.5573	0.7458	−0.0349	0.088
0.8904	1.5644	0.7804	−0.0239	0.055
0.9305	1.5683	0.8017	−0.0158	0.036
$(x)CH_2Cl_2 + (1 - x)CHCl_3$				
0.0633	1.4623	0.5040	−0.0003	−0.009
0.1191	1.4548	0.4976	0.0000	−0.011
0.1924	1.4447	0.4892	0.0003	−0.015
0.3101	1.4278	0.4741	−0.0008	−0.021
0.3607	1.4203	0.4686	−0.0003	−0.025
0.4299	1.4097	0.4602	−0.0005	−0.026
0.5221	1.3951	0.4501	0.0004	−0.030
0.6464	1.3743	0.4352	0.0003	−0.028
0.6833	1.3678	0.4301	−0.0005	−0.023
0.7400	1.3578	0.4236	−0.0002	−0.025
0.7979	1.3471	0.4163	−0.0006	−0.017
0.8681	1.3339	0.4083	−0.0003	−0.015
0.9034	1.3270	0.4040	−0.0004	−0.010
0.9358	1.3206	0.4005	0.0000	−0.007
$(x)(1{:}1(CCl_4 + CH_2Cl_2)) + (1 - x)CHCl_3$				
0.0518	1.4701	0.5128	−0.0003	0.000
0.1221	1.4695	0.5144	−0.0006	0.004
0.2058	1.4688	0.5168	−0.0003	0.007
0.2588	1.4685	0.5185	0.0000	0.001
0.3510	1.4678	0.5212	0.0003	0.001
0.4986	1.4668	0.5247	0.0000	−0.005
0.5428	1.4665	0.5260	0.0002	−0.007
0.6767	1.4658	0.5292	−0.0001	−0.025
0.7058	1.4656	0.5302	0.0002	−0.026
0.7365	1.4654	0.5306	−0.0002	−0.028
0.8266	1.4647	0.5334	0.0003	−0.027
0.8882	1.4642	0.5347	0.0000	−0.025
0.9317	1.4637	0.5361	0.0003	−0.016

tion-proof. All masses were corrected to vacuum. The precision and accuracy for mole fraction could be better than 0.0001.

Viscosities were measured with one Ubbelohde type glass capillary tube viscosimeter with a capacity of 2.1 cm^3 . The capillary tube is 11.8 cm long with a diameter of 0.39 mm. The viscosity can be expressed as

$$\eta/\rho = at - b/t \tag{1}$$

where ρ is the density of a liquid, t is the time for flow, and a and b are the viscosimeter parameters. The a and b parameters were obtained by measurements on water at (20, 25, and 30 °C).[18] The obtained parameters are $a = 0.003\,258$ and $b = 0.6200$. The temperature of the thermostat was controlled to ±0.002 K. The experimental temperature was (303.15 ± 0.01) K. An electrical stopwatch with a precision of 0.01 s was used. The repeatability for reading was ±0.05 s. At least three time recordings reproducible to 0.05 s were obtained, and the average value was used. It could be expected that the measurement of viscosity has a precision of 0.05%. The uncertainty is ±0.2%.

The densities of solutions were measured with an Anton Paar 45 densimeter with a precision of $\pm 5 \times 10^{-5}$ g·cm^{-3} and an accuracy of 0.005%. It was calibrated with deionized double-distilled water and dry air.

3. Results and Discussion

The viscosities η, densities ρ, viscosity deviations $\Delta\eta$, and excess molar volumes V^E for the binary and ternary mixtures are presented in Table 2.

The relation of $\Delta\eta$ or V^E to the mole fraction of one of the two components could be represented by one of the following correlating equations:

$$Y^E = x(1 - x)\sum_{i=0}^{n} A_i(1 - 2x)^i \tag{2}$$

$$Y^E = x(1 - x)\sum_{i=0}^{n} A_i x^{i/2} \tag{3}$$

where Y^E represents $\Delta\eta$ or V^E. The coefficients in eqs 2 and 3 were obtained by equal weighting least-squares regression. The coefficients and the standard deviations are presented in Table 3.

Figure 1 was plotted to show the relations of $\Delta\eta$ or V^E values to molar fractions. Part a is for $\Delta\eta$ values, and part b is for V^E values. The $\Delta\eta$ values for chloroform + dichloromethane and 1:1(carbon tetrachloride + dichloromethane) + chloroform are rather small and could also be considered to be zero, so it is not necessary to correlate them and to plot them in the figure.

Although there are no literature values at 303.15 K for comparison, the temperature influence on V^E is so small that the literature values around 303.15 K could be employed for an approximate comparison. For CCl_4 +

Table 3. Values of the Coefficients in Eq 2 or Eq 3 and the Standard Deviations

	A_0	A_1	A_2	$\sigma(\Delta\eta)$ mPa·s	$\sigma(V^E)$ cm^3·mol^{-1}	eq used
$(x)CCl_4 + (1-x)CH_2Cl_2$	−0.4993	0.2583		0.0002		3[a]
	1.180	0.063			0.002	2
$(x)CCl_4 + (1-x)CHCl_3$	−0.2077	0.0441		0.0004		2
	0.649	0.052	−0.067		0.002	2
$(x)CH_2Cl_2 + (1-x)CHCl_3$	0					
	−0.115				0.002	2
$(x)(1{:}1(CCl_4 + CH_2Cl_2)) + (1-x)CHCl_3$	0					
	−0.028	0.167	−0.131		0.002	2

[a] Here $(1-x)$ is taken for x in the regression.

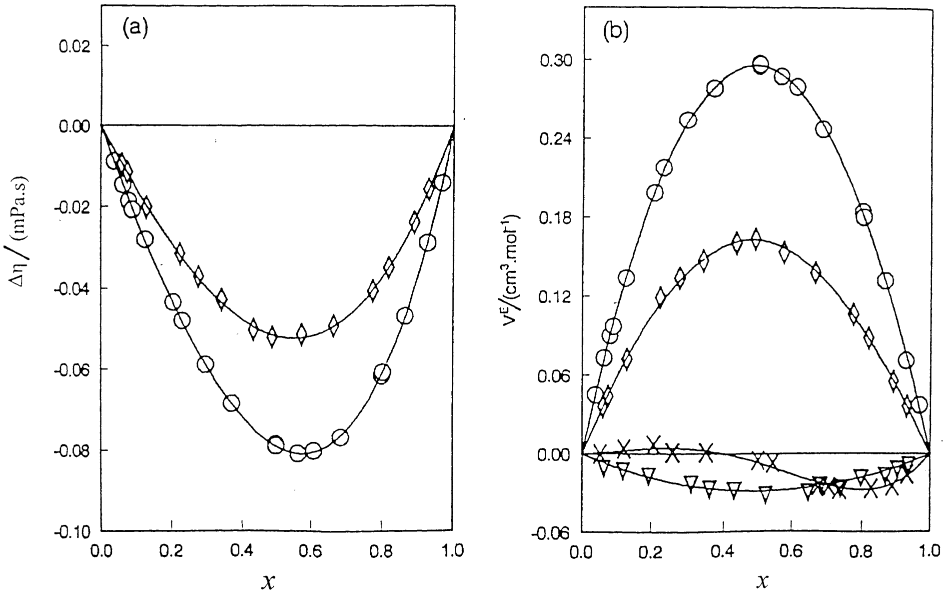

Figure 1. Viscosity deviation (a) and molar excess volume V^E (b) at 303.15 K for (○) $(x)CCl_4 + (1-x)CH_2Cl_2$, (◇) $(x)CCl_4 + (1-x)CHCl_3$, (▽) $(x)CH_2Cl_2 + (1-x)CHCl_3$, and (×) $(x)(1{:}1(CCl_4 + CH_2Cl_2)) + (1-x)CHCl_3$.

$CHCl_3$, the present V^E values are smaller than those at 298.15 K by McGlashan et al.[10] with an average difference of 0.010 cm^3·mol^{-1}, and the difference is 0.009 cm^3·mol^{-1} at the equimolar composition. The present V^E values are smaller than those at 298.15 K by Artal et al.[12] with an average difference of 0.015 cm^3·mol^{-1}, and the difference is 0.013 cm^3·mol^{-1} at the equimolar composition. There is no obvious difference between the present V^E values and those at 308.15 K by Niigam and Singh.[11] By checking the V^E values for $CCl_4 + CHCl_3$ at 308.15 K, 313.15 K, and 318.15 K by Niigam and Singh,[11] it can be found that the V^E values decrease with the increase of temperature by an average value of 0.006 cm^3·mol^{-1} every 5 K. So the comparing results are satisfactory. For $CHCl_3 + CH_2Cl_2$, the present V^E values are a little more negative than those at 298.15 K by Artal et al.[12] with an average difference of 0.004 cm^3·mol^{-1}, and the difference is 0.007 cm^3·mol^{-1} at the equimolar composition. The V^E values themselves are small for this system. For $CCl_4 + CH_2Cl_2$, the present V^E values are smaller than those at 298.15 K by Artal et al.[12] with an average difference of 0.010 cm^3·mol^{-1}, and the difference is 0.006 cm^3·mol^{-1} at the equimolar composition. The present V^E values are smaller than those at 298.15 K by Compostizo et al.[13] with an average difference of 0.016 cm^3·mol^{-1} and the difference is 0.011 cm^3·mol^{-1} at the equimolar composition.

The V^E values for $CCl_4 + CH_2Cl_2$ and $CCl_4 + CHCl_3$ are positive. The V^E values for $CCl_4 + CH_2Cl_2$ are obviously larger than those for $CCl_4 + CHCl_3$. It could be assumed that this is caused mainly by two reasons: (1) Nonpolar CCl_4 interacts weakly with polar CH_2Cl_2 and polar $CHCl_3$. The polarity of CH_2Cl_2 is larger than that of $CHCl_3$. (2) The molecules have different sizes and shapes. For example, CCl_4 is spherical.

The V^E values for $CHCl_3 + CH_2Cl_2$ are negative with a small magnitude over the entire composition range. On the first view, it could be predicted that there is a specific interaction between CH_2Cl_2 and $CHCl_3$, most possibly the dipole−dipole interaction.

On the basis of the V^E values of the three binary mixtures, it could also be discovered that the polarity of one molecule plays a key role in molecular interactions.

From another viewpoint, the pronounced positive V^E values for $CCl_4 + CH_2Cl_2$ and $CCl_4 + CHCl_3$ may perhaps come from the fact that the "most compact packing of spherical CCl_4" is destroyed by mixing with the aspherical molecule CH_2Cl_2 or $CHCl_3$.

For $1{:}1(CCl_4 + CH_2Cl_2) + CHCl_3$, the V^E values are rather small when $x_{CHCl_3} > 0.5$ and a little negative when $x_{CHCl_3} < 0.5$. It may be assumed that the definition of pseudochloroform is meaningful. Also it could be shown that there is a stronger interaction between CH_2Cl_2 and $CHCl_3$ than that between CCl_4 and CH_2Cl_2 and/or $CHCl_3$.

For $CCl_4 + CH_2Cl_2$ and $CCl_4 + CHCl_3$, the values are negative over the entire composition range. The values for $(CCl_4 + CH_2Cl_2)$ are obviously more negative than those for $(CCl_4 + CHCl_3)$. These may suggest that different sizes, shapes, and polarities between CCl_4 and CH_2Cl_2 or $CHCl_3$ could be the main factors to cause the negative viscosity deviations. Also, the molecular interactions between CCl_4

and CH_2Cl_2 or $CHCl_3$ are weaker than those in their pure components. The fact that the "most compact packing of spherical CCl_4" is destroyed is perhaps the main factor for the reduced viscosities after mixing. For $CHCl_3 + CH_2Cl_2$, the $\Delta\eta$ values are close to zero. This may indicate that the measuring precision is rather ideal. This system behaves as an ideal mixing in terms of viscosity. Perhaps this could be explained by the fact that the differences of size, shape, and polarity between $CHCl_3$ and CH_2Cl_2 are small and also by the fact that the interactions between $CHCl_3$ and CH_2Cl_2 are near the average of the interactions in their pure states. For 1:1($CCl_4 + CH_2Cl_2$) + $CHCl_3$, the $\Delta\eta$ values are also close to zero. This could further confirm the definition of pseudochloroform.

4. Conclusion

On the basis of the results and discussion above, the strength of interaction between molecules in the binary mixtures decreases in order CH_2Cl_2 - - - $CHCl_3$ > CCl_4 - - - CH_2Cl_2 > CCl_4 - - - $CHCl_3$. There are very weak specific interactions between CCl_4 and CH_2Cl_2 or between CCl_4 and $CHCl_3$. There is a relatively stronger specific interaction between $CHCl_3$ and CH_2Cl_2. The 1:1($CCl_4 + CH_2Cl_2$) + $CHCl_3$ behaves equal to chloroform in many aspects, for example, viscosity and volume. So it could be defined as pseudochloroform.

Literature Cited

(1) Zhang, H. L.; Han, S. J. Interaction Studies from Viscometric and Volumetric Behaviour of Binary Systems of Chlorinated Methanes with Normal alkanols at 303.15 K. *Phys. Chem. Liq.* **1996**, *31*, 49−62.
(2) Zhang, H. L.; Han, S. J. Viscometric and Volumetric Studies on Binary Mixtures of 1,2-Dichloroethane and Chlorinated Methanes or Their Binary Equimolar Mixtures at 303.15 K. *Fluid Phase Equilib.* **1997**, *140*, 233−244.
(3) Singh, P. P. Topological Investigations of the Viscous Behaviour of Binary Mixtures of Nonelectrolytes. *Ind. J. Chem.* **1988**, *27A*, 469−473.
(4) Singh, P. P.; Bhatia, M.; Maken, S. Topological Investigations of the Viscous Behaviour of Some Binary Mixtures of Nonelectrolytes: Part 2. *Ind. J. Chem.* **1990**, *29A*, 263−266.
(5) Grunberg, L.; Nissan, A. H. Mixture Law for Viscosity. *Nature* **1949**, *164*, 799−800.
(6) Fort, R. J.; Moore, W. R. Viscosities of Binary Liquid Mixtures. *Trans. Faraday Soc.* **1966**, *62*, 1112−1119.
(7) Nigam, R. K.; Mahl, B. S. Strength of Interactions in Binary Mixtures of Methylene Chloride with Benzene, Toluene & Xylenes; Chloroform with Acetone, Ether & Dioxane; Benzene with Acetone, *n*-Pentane & *n*-Hexane; & of Cyclohexane with *n*-Pentane. *Ind. J. Chem.* **1971**, *9*, 1255−1258.
(8) Nath, J.; Singh, G. Binary Systems of 1,2-Dichloroethane with Benzene, Toluene, *p*-Xylene, Quinoline, and Cyclohexane. 4. Viscosities at 303.15 K. *J. Chem. Eng. Data* **1988**, *33*, 58−60.
(9) Katti, P. K.; Chaudhri, M. M. Viscosities of Binary Mixtures of Benzyl Acetate with Dioxane, Aniline, and *m*-Cresol. *J. Chem. Eng. Data* **1964**, *9*, 442−443.
(10) McGlashan, M. L.; Prue, J. E.; Sainsbury, I. E. J. Equilibrium Properties of Mixtures of carbon Tetrachloride and Chloroform. *Trans. Faraday Soc.* **1954**, *50*, 1284−1296.
(11) Nigam, R. K.; Singh, P. P. Excess Volume of Mixing. *Trans. Faraday Soc.* **1964**, *65*, 950−961.
(12) Artal, M.; Munoz Embid, J.; Velasco, I.; Otin, S. Excess Volumes of (1-Chlorobutane or 1,2-Dichloroethane or Tetrachloromethane or 1,1,2,2-Tetrachloroethane + Dichloromethane or Trichloromethane) and of (Dichloromethane+Trichloromethane) at the Temperature 298.15 K. *J. Chem. Thermodyn.* **1991**, *23*, 1131−1134.
(13) Compostizo, A.; Cresp Colin, A.; Vigil, M. R.; Rubio, R. G.; Diaz Peña, M. Pressure dependence of the Excess Properties of Simple Molecular Mixtures. The $CCl_4 + CH_2Cl_2$ System. *J. Phys. Chem.* **1991**, *95*, 319−324.
(14) Joshi, S. S.; Aminabhavi, T. M.; Shukla, S. S. Densities and Shear Viscosities of Anisole with Nitrobenzene, Chlorobenzene, Carbon Tetrachloride, 1,2-Dichloroethane, and Cyclohexane from 25 to 40. *J. Chem. Eng. Data* **1990**, *35*, 247−253.
(15) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents, Physical Properties and Methods of Purification*, 4th ed.; Wiley-Interscience: New York, 1986.
(16) Acevedo, I. L.; Katz, M. Viscosities and Thermodynamics of Viscous Flow of Some Binary Mixtures at Different Temperatures. *J. Solution Chem.* **1990**, *19*, 1041−1052.
(17) Takenaka, M.; Tanaka, R.; Murakami, S. Determination of the Excess Volumes of (Cyclohexane+Benzene) between 298.15 and 303.15 K by Use of a Vibrating Densimeter. *J. Chem. Thermodyn.* **1980**, *12*, 849−855.
(18) Stokes, R. H.; Mills, R. *The International Encyclopedia of Physical Chemistry and Chemical Physics. Vol.: Viscosity of Electrolytes and Related Properties*; Pergamon Press: New York, 1965; p 74.

Received for review April 10, 2002. Accepted September 16, 2002.

JE020067X