Interaction in Nonelectrolyte Solutions

Solubility of Naphthalene at 25° in Some Mixed Nonaromatic Solvents

E. L. HERIC and CECIL D. POSEY
University of Georgia, Athens, Ga.

The solubility of naphthalene has been determined at 25° in the six binary mixed solvents from among carbon tetrachloride, cyclohexane, *n*-hexane, and *n*-hexadecane. The determinations were made refractometrically under isothermal conditions. The average uncertainty in the solubilities is less than 0.001 in mole fraction naphthalene. Interaction in the ternary systems is related to that of the component pairs, using the approaches of Hildebrand and Guggenheim. The average errors in correlation by either approach are comparable, 0.001 to 0.002 in mole fraction naphthalene, for those systems of known solvent-solvent interaction effects. Deviations from the Hildebrand and Guggenheim equations are related to ternary interaction terms for those systems in which all interactions between component pairs are known. Apparent solvent-solvent interactions obtained by present ternary solubility studies are compared with literature values based upon studies of the binary systems. The error introduced by approximating the interaction of a component pair in terms of the interaction of each member of the pair with a third component is considered. The approximation results in larger errors in the hexadecane systems than in the other systems. A summary of the results in the series of twenty-one systems, included in the continuing study, is presented.

THIS is the third, and concluding, part of a series concerning interactions in the ternary systems formed by naphthalene and benzene, toluene, ethylbenzene, carbon tetrachloride, cyclohexane, *n*-hexane, and *n*-hexadecane. The first part (*3*) dealt with the six systems containing benzene as a common solvent component, and the second part (*4*) with nine additional systems containing toluene or ethylbenzene. The present paper describes work on the remaining six solvent pairs, those which do not include an aromatic solvent.

Work on the total of twenty-one mixed solvent systems is consistent in approach and techniques. Frequent reference will be made to the previously reported (*3, 4*) studies for a description of the experimental methods and a comparison of the results found there with those in the present systems. To promote clarity, the numbering of the equations used in reporting the benzene systems will be maintained.

EXPERIMENTAL

The interaction effects were investigated by determination of the solubility of naphthalene in the mixed solvent systems. A description of the reagents, equipment, and experimental procedures has been given (*3*).

RESULTS

Columns 4 and 5 of Table I list the experimental naphthalene solubilities corresponding to the initial solvent compositions given in Columns 2 and 3. The solubilities are also expressed analytically in terms of deviation from a linear dependence of naphthalene solubility on solvent composition, the latter expressed as mole fraction in the solvent mixture—i.e., on a solute-free basis. The deviations [Equation 11, (*3*)]

$$D = x_1^0x_3^0[a + b(x_1^0 - x_3^0) + c(x_1^0 - x_3^0)^2] \qquad (11)$$

are without theoretical significance, and are used only as a convenient means of summarizing the solubility results. The constants of the deviation functions (Table II) have been determined by least-squares treatment of the experimental solubilities. The maximum difference between experimental solubilities and those obtained with Equation 11 is 0.001 mole fraction naphthalene.

The activity coefficient of the solute, component 2, in the ternary systems may be expressed in terms of a mole fraction dependence, Equation 12, (*2*),

$$RT\ln\gamma_2 = x_1^2W_{12} + x_3^2W_{23} + x_1x_3\,(W_{12} + W_{23} - W_{13}) \qquad (12)$$

or a volume fraction dependence, Equation 13, (*5*).

$$RT\ln\gamma_2 = V_2^0[\phi_1^2W'_{12} + \phi_3^2W'_{23} + \phi_1\phi_3(W'_{12} + W'_{23} - W'_{13}] \qquad (13)$$

Equation 13 may also be modified by the inclusion of Flory-Huggins entropy (*5*). Comparison (in terms of solubilities) of γ_2, predicted with Equations 12 and 13 and the experimental values, is given in Columns 6 and 7 (Table I), respectively. Solvent-solvent W values used in Equation 12, listed in Column 1 of Table III, are those reported at $x = 0.5$. Corresponding W' used in Equation 13 have been calculated from W values at that composition. The former are listed in Column 5 of Table III. Literature values of W are available for only three of the present systems, and for these the average errors by Equations 12 and 13 are comparable, 0.002 to 0.001 in mole fraction naphthalene.

Column 8 of Table I lists the comparisons between experimental solubilities and those obtained via Equation 13, assuming the approximation of Equation 15 for the solvent-solvent interaction. The solvent-solvent W' values obtained with Equation 15 (*3*),

$$|W'_{13}|^{1/2} = |W'_{12}|^{1/2} \pm |W'_{23}|^{1/2} \qquad (15)$$

are listed in Column 9 of Table III. [For comparison, the square of the difference between the solubility parameters

Table I. Solubility of Naphthalene in Mixed Solvents

	Initial Solvent Composition		Exptl. Naphthalene Solubility		10^3(Exptl. Solubility − Calcd. Solubility)		
Solvent Pair	Mole fraction of 1st-named solvent	Volume fraction of 1st-named solvent	Mole fraction	Volume fraction	Equation 12	Equation 13	Equation 13, with assumption of Equation 15
Carbon tetrachloride–hexane	0.9017	0.8712	0.2447	0.282	...	...	0
	0.7997	0.7466	0.2298	0.261	...	...	0
	0.5971	0.5223	0.1978	0.214	...	...	0
	0.4315	0.3590	0.1742	0.182	...	...	0
	0.2029	0.1581	0.1415	0.140	...	...	0
	0.0221	0.0164	0.1191	0.112	...	...	0
Carbon tetrachloride–cyclohexane	0.7630	0.7419	0.2356	0.275	0	0	−1
	0.5883	0.5606	0.2169	0.250	0	0	0
	0.3971	0.3703	0.1955	0.223	0	1	0
	0.1939	0.1768	0.1723	0.194	0	1	1
Carbon tetrachloride–hexadecane	0.8410	0.6378	0.2282	0.221	...	...	−12
	0.5820	0.3150	0.2058	0.151	...	...	−16
	0.4057	0.1840	0.2009	0.126	...	...	−13
	0.1517	0.0558	0.2003	0.104	...	...	−7
Hexane-cyclohexane	0.7986	0.8275	0.1255	0.122	0	1	3
	0.6013	0.6460	0.1319	0.132	0	1	3
	0.3996	0.4461	0.1396	0.144	0	1	4
	0.1553	0.1820	0.1453	0.157	0	1	2
Hexane-hexadecane	0.8511	0.7189	0.1348	0.109	3	−1	−5
	0.5882	0.3899	0.1597	0.105	11	−2	−9
	0.3964	0.2271	0.1743	0.102	9	−4	−10
	0.1573	0.0771	0.1924	0.0984	4	−2	−5
Cyclohexane-hexadecane	0.8289	0.6417	0.1542	0.138	...	...	−12
	0.5736	0.3322	0.1680	0.117	...	...	−16
	0.4181	0.2099	0.1779	0.109	...	...	−13
	0.4067	0.2022	0.1785	0.109	...	...	−13
	0.1689	0.0699	0.1935	0.101	...	...	−6
Av. dev.					2	1	5

Table II. Constants of Deviation Functions, Equation 11

Solvent Pair	10^3a	10^3b	10^3c
Carbon tetrachloride–hexane	−17	15	2
Carbon tetrachloride–cyclohexane	12	1	6
Carbon tetrachloride–hexadecane	−114	−54	−31
Hexane-cyclohexane	13	−1	2
Hexane-hexadecane	25	17	7
Cyclohexane-hexadecane	−14	−16	−6

x_1^0 in Equation 11 refers to the 1st-named solvent in each solvent pair.

of the various solvent pairs, equal to W'_{13} by solubility parameter theory (*5*), has been listed in Column 10 of Table III. The solubility parameters are from Column 8 of Table III (*3*).] The assumption of Equation 15 results in an average error of 0.004 in mole fraction naphthalene for the three systems of known solvent-solvent interaction. For all six systems, the average error is 0.005. The validity of the approximation in Equation 15 is also shown in Figures 1 through 4, which are based on a Flory-Huggins entropy. Modification to Raoult entropy has no consistent effect on the plots. In these figures, previous systems have been included for comparison (*3, 4*).

Equations 12 and 13 have been used for the determination of apparent solvent-solvent interaction from measurements in the ternary systems. Columns 2 and 6 of Table III contain the results by the respective equations. The corresponding mean in each system is given in Columns 3 and 7, and the comparison of the mean with the literature value is indicated in Columns 4 and 8. The order of listing in each system in Table III is the same as that in Table I.

A relationship between system composition and the deviations of experimental $\overline{\Delta G_2^E}$ from those predicted with Equations 12 or 13 is possible for the 10 systems for which literature values of W_{13} exist. Of these, however, the estimated uncertainty in literature W_{13} is larger than the effect sought in four systems, and, in two others, the deviations of experimental results from predicted values are zero. The remaining four systems are presented in Table IV, where the deviations are assumed to result from ternary interaction. It could also be argued that the deviations are caused by terms in $(x_i - x_j)^n$ in Equation 1. The data are insufficient in number to resolve this uncertainty. It is assumed here that per mole of mixture, using mole fraction as the concentration variable,

$$\Delta G^E = x_1x_2W_{12} + x_1x_3W_{13} + x_2x_3W_{23} + x_1x_2x_3W_{123}$$

or

$$\Delta G^E = \Delta G^E_{\text{binary},\,x} + x_1x_2x_3W_{123} \qquad (18)$$

where $\Delta G^E_{\text{binary},\,x}$ is the sum of the binary interaction terms. By partial differentiation of Equation 18

$$\overline{\Delta G_2^E} = \overline{\Delta G_2^E}_{\text{binary},\,x} + x_1x_3(1 - 2x_2)W_{123} \qquad (19)$$

where $\overline{\Delta G_2^E}_{\text{binary},\,x}$ is RT in γ_2 calculated with Equation 12. Similarly, one may obtain

$$\overline{\Delta G_2^E} = \overline{\Delta G_2^E}_{\text{binary},\,\phi} + V_2^0\phi_1\phi_3(1 - 2\phi_2)W'_{123} \qquad (20)$$

where $\overline{\Delta G_2^E}_{\text{binary},\,\phi}$ is RT ln γ_2 calculated with Equation 13. The sequence of points in each system is the same as that given in Tables IV (*3*) and I. Except for the hexane–hexadecane system, the predicted solubilities and solvent molal volumes are sufficiently similar that only mole fraction as concentration variable has been considered. The probable errors given in Table IV are based upon the uncertainties in the experimental values of the mole fractions of the various components.

DISCUSSION

Table I shows that, except for the carbon tetrachloride–hexadecane system, naphthalene solubility (as mole fraction) decreases continually from the solvent of greater to the solvent of lesser solvent action toward the solute. In the former system, the solubility passes through a minimum in hexadecane-rich solvent mixtures. The average departure of experimental solubilities from the smoothed values is comparable to that found in previous work (*3, 4*).

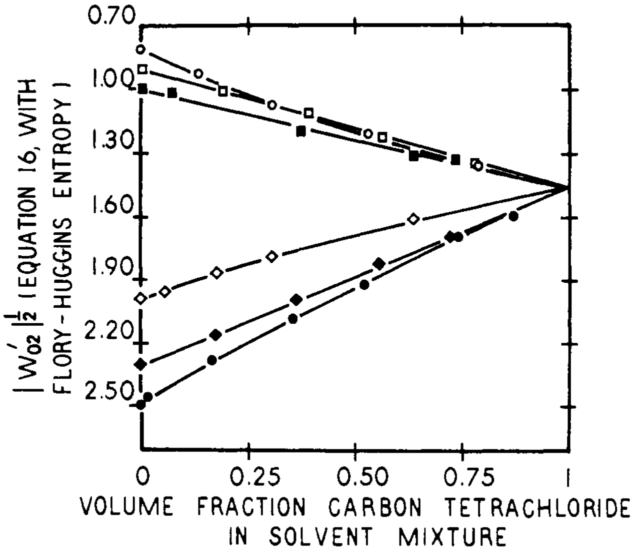

Figure 1. $|W'_{02}|^{1/2}$ in mixed solvents containing carbon tetrachloride

■ carbon tetrachloride-benzene
□ carbon tetrachloride-toluene
○ carbon tetrachloride-ethylbenzene
● carbon tetrachloride-hexane
◆ carbon tetrachloride-cyclohexane
◇ carbon tetrachloride-hexadecane

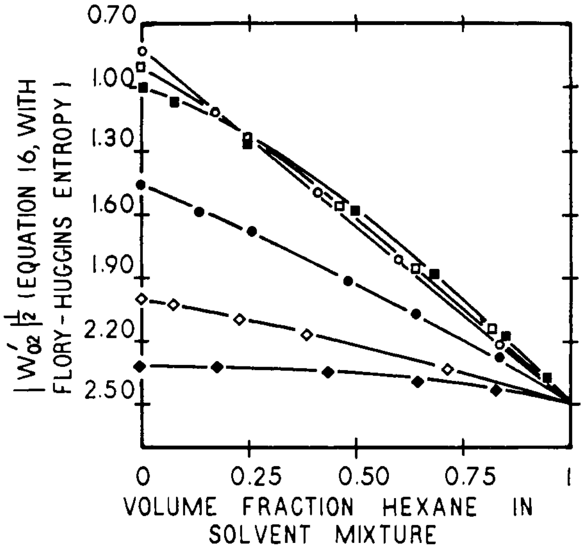

Figure 2. $|W'_{02}|^{1/2}$ in mixed solvents containing hexane

■ hexane-benzene
□ hexane-toluene
● hexane-carbon tetrachloride
○ hexane-ethylbenzene
◆ hexane-cyclohexane
◇ hexane-hexadecane

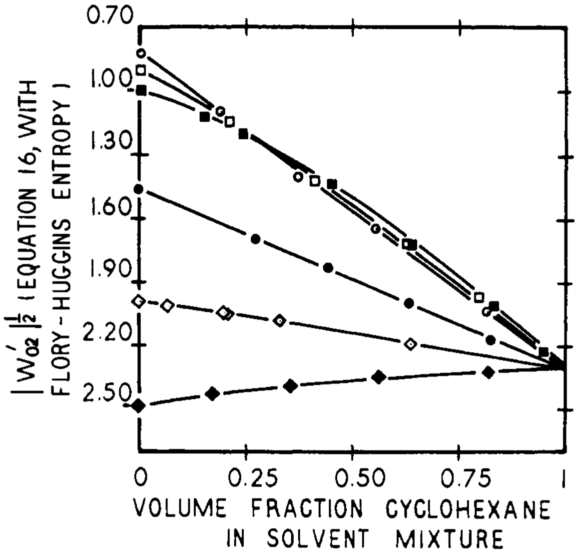

Figure 3. $|W'_{02}|^{1/2}$ in mixed solvents containing cyclohexane

■ cyclohexane-benzene
□ cyclohexane-toluene
● cyclohexane-carbon tetrachloride
○ cyclohexane-ethylbenzene
◆ cyclohexane-hexane
◇ cyclohexane-hexadecane

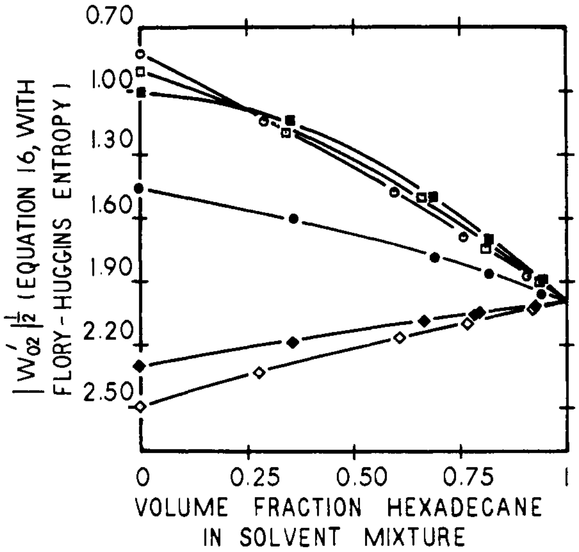

Figure 4. $|W'_{02}|^{1/2}$ in mixed solvents containing hexadecane

■ hexadecane-benzene
□ hexadecane-toluene
● hexadecane-carbon tetrachloride
○ hexadecane-ethylbenzene
◆ hexadecane-cyclohexane
◇ hexadecane-hexane

In the hexane-hexadecane system, the errors by Equations 12 and 13 are of opposite sign and those by the latter are significantly smaller. In the other two systems, where the comparison can be made the results are quite similar, within 0.001 mole fraction naphthalene of the experimental values. The rather large average error of 0.005 in mole fraction naphthalene via Equation 15 (Column 8, Table I) results essentially from the behavior of the three hexadecane-solvent systems, in which the average error is 0.011. The systematic trend to increased error in the various systems in Table I, as equimolal solvent composition is approached, indicates that the cause is not experimental error.

A comparison of : W'_{13} obtained with Equation 15, those predicted with solubility parameters (*5*), and those calculated from the molar excess Gibbs free energy of mixing in binary systems may be made respectively with Columns 9, 10, and 5 of Table III, in the three systems where the comparison is possible. (A measure of the differences is that in a binary system of near equal volume fractions, 0.1 in W' is equivalent to about 10 cal. mole^{-1} in W, or to a change of about 0.5% in the activity coefficient of the present solute.) Apparently, no consistent relation obtains between the W'_{13} obtained by the three different methods.

The W_{13} values, obtained by the application of Equation 12 to the solubility determinations in the present ternary systems (Columns 2 to 4, Table III), show variable agree-

Table III. Solvent-Solvent Interaction Energies

W (Cal. Mole^{-1})				W' (Cal. Ml.$^{-1}$)					
Literature	Exptl. Equation 12	Mean ± av. dev. exptl.	Literature − exptl.	Literature[d]	Exptl. Equation 13	Mean ± av. dev. exptl.	Literature − exptl.	Equation 15	$(\delta_1 - \delta_3)^2$ from ideal energies of vaporization[e]
CARBON TETRACHLORIDE–HEXANE									
	18	14 ± 8			1.08	1.21 ± 0.14		1.17	1.74
	13				0.97				
	12				1.17				
	7				1.20				
	1				1.34				
	36				1.48				
CARBON TETRACHLORIDE–CYCLOHEXANE									
67.2[a]	63	70 ± 8	−3	0.654	0.68	0.74 ± 0.04	−0.09	0.81	0.15
	67				0.72				
	63				0.75				
	87				0.80				
CARBON TETRACHLORIDE–HEXADECANE									
	−600	−433 ± 88			−1.69	−2.59 ± 0.62		0.048	0.36
	−442				−2.24				
	−372				−2.64				
	−320				−3.77				
HEXANE-CYCLOHEXANE									
67[b]	67	67 ± 1	0	0.563	0.84	0.78 ± 0.06	−0.22	0.032	0.86
	66				0.85				
	66				0.74				
	70				0.70				
HEXANE-HEXADECANE									
−70[c]	237	152 ± 42	−222	−0.385	−0.49	−0.92 ± 0.30	0.54	0.74	0.52
	162				−0.74				
	129				−1.06				
	100				−1.37				
CYCLOHEXANE-HEXADECANE									
	−97	−40 ± 24			−1.67	−2.13 ± 0.23		0.46	0.044
	−47				−2.03				
	−29				−2.20				
	−27				−2.22				
	−3				−2.55				

[a] References *7, 8.* [b] References *6, 7.* [c] References *1, 7.* [d] From literature w, using ϕ which obtain at $x = 0.5$. [e] 1 = first-named solvent. 3 = second-named solvent.

Table IV. Ternary Interaction Constants

	$10^2 W_{123}$ (Cal. Mole^{-1}), by Equation 19	
Solvent Pair	Exptl. ± estimated prob. error	Mean ± estimated prob. error of the mean
Benzene–toluene	0.0 ± 1.0	
	1.1 ± 0.42	
	1.2 ± 0.30	
	0.81 ± 0.30	
	0.42 ± 0.32	0.83 ± 0.16
Benzene–carbon tetrachloride	1.6 ± 0.4	
	1.7 ± 0.3	
	1.5 ± 0.4	
	1.3 ± 0.5	1.6 ± 0.1
Benzene–cyclohexane	−2.3 ± 1.3	
	−1.7 ± 0.4	
	−1.5 ± 0.4	
	−1.3 ± 0.3	
	−1.4 ± 0.4	
	−0.0 ± 1.1	−1.4 ± 0.1
Hexane-hexadecane	−1.9 ± 0.5	
	−3.6 ± 0.3	
	−3.0 ± 0.3	
	−2.4 ± 0.5	−3.0 ± 0.3
Hexane-hexadecane[a]	0.28 ± 0.23[a]	
	0.40 ± 0.16[a]	
	0.98 ± 0.22[a]	
	1.1 ± 0.44[a]	0.56 ± 0.17[a]

[a] Values are for W'_{123} cal. ml.$^{-1}$ per Equation 20.

ment with the three literature values. Thus, in the carbon tetrachloride- and hexane–cyclohexane systems the agreement is excellent, within 5 cal. mole^{-1}, and the average deviation from the mean W_{13} is small. The former binary system has been shown to adhere closely to *s*-regular behavior (*2*). The very large departure of the experimental W_{13} in the hexane–hexadecane system from the literature value (*1*) is in sharp contrast to the foregoing. This error is about 3 times as great as the next largest, that encountered in the benzene–carbon tetrachloride system (*3*). That W_{13} was found to have a negative value in the study of the hexane–hexadecane binary system (*1*), however, indicates the interaction there departs rather considerably from that proposed for regular solutions. Thus, disagreement between present experimental and literature values is not surprising. The average deviation of experimental W_{13} from the mean for the six present systems is small except where there is a trend in W_{13} with varying mixed solvent composition. W'_{13} calculated with Equation 13, and the solubility measurements in the ternary systems (Columns 6 to 8, Table III) show a behavior similar to that noted for W_{13}.

The W_{123} values (Table IV) are of the same order of magnitude as most of the W_{ij} noted in the study. While the W_{123} are relatively constant in a system, this constancy has been obtained under conditions of relatively fixed x_2 values. Greater validity of the results must depend on experimental methods which allow wider latitude in the variation of the concentrations of all three components.

In the hexane-hexadecane-naphthalene system, there is evidence of some systematic trend in the variation of W_{123}, and this is yet more pronounced in the behavior of W'_{123}.

SUMMARY OF RESULTS IN THE TWENTY-ONE MIXED SOLVENT SYSTEMS

There are three major aspects to this series of studies:

Use of Equations 12 or 13 in Predicting Interaction. In the 10 systems for which literature values of solvent-solvent interaction are available, the average error in the prediction of solubility by either equation is 0.002 mole fraction naphthalene. In a given system, component dissimilarity is reflected in the size of the error.

Use of Equations 15 or 16 in Approximating Interaction. Treatment of a ternary system as a pseudo-binary with Equation 16 is often a useful approach. The approximation that 1–3 component interaction may be related to that of 1–2 and 2–3 by Equation 15 is similarly available. The use of these equations appears to be most valid for the aromatic pairs. Fair agreement is found for the nonaromatic pairs, while for aromatic-nonaromatic pairs, there is frequently considerable error. The assumption is generally poorest for systems involving hexadecane.

Determination of Binary Interchange Energy by Measurements in a Ternary System. In some of the systems, agreement between experimental and literature values of solvent-solvent interchange energy is quite good. Thus, the determination of that quantity by solubility measurements in solvent-solvent mixtures is a suitable method in systems behaving regularly and with pairwise interaction.

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NOMENCLATURE

ΔG^E = molar excess Gibbs free energy of mixing
$\overline{\Delta G}_2^E$ = solute partial molar excess Gibbs free energy of mixing
$\overline{\Delta G}^E_{2\text{binary},\,x}$ = $\Delta\overline{G}_2^E$ calculated with Equation 12
$\overline{\Delta G}^E_{2\text{binary},\,\phi}$ = $\Delta\overline{G}_2^E$ calculated with Equation 13
$V°$ = molar volume
W = interchange energy, cal. mole^{-1}
W' = interchange energy, cal. ml.$^{-1}$
x = mole fraction
$x°$ = mole fraction, solute-free basis
δ = solubility parameter
γ = activity coefficient
ϕ = volume fraction
$\phi°$ = volume fraction, solute-free basis

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Conductivity of Silver Nitrate in Nonaqueous and Mixed Solvents

R. E. BUSBY
Brunel College, Woodlands Avenue, Acton, London, W. 3

V. S. GRIFFITHS
Battersea College of Technology, Battersea, London, S.W. 11.

Measurements of the conductivity of silver nitrate in methanol and binary mixtures of methanol containing 0.1 mole % of nitromethane, pyridine, and benzene at 30° C. are reported and discussed.

SOLVENT-ION EFFECTS have been observed in previous conductivity work (*1*) at 25° C. with silver nitrate in methanol containing an electron-donating additive, present in an amount (0.1 mole %) sufficient to interact appreciably with the cation but not to alter the viscosity and dielectric constant of the main solvent effectively. The conductivity of silver nitrate in methanol and binary solvent mixtures was measured at 30° C. Each mixture contained 99.9 mole % methanol and 0.1 mole % of one of the additives used previously (*1*), namely, pyridine, nitromethane, and benzene. This provided thermodynamic data to extend knowledge on solvent-ion interaction.