

CHAPTER - XI

Ion-Solvent and Ion-Ion Interactions of Phosphomolybdic Acid in Aqueous Solution of Catechol at 298.15, 308.15 and 318.15K

11.1. Introduction

Studies on densities (ρ) and viscosities (η) of solutions are of great importance in characterizing the properties and structural aspects of solutions.. Hence studies on the limiting apparent molar volume and viscosity- B coefficients of electrolyte provide us valuable information regarding ion-ion, ion-solvent and solvent-solvent interactions ¹⁻³. It has been found by a number of workers ⁴⁻⁶ that the addition of a solute could either make or break the structure of a liquid. As the viscosity of a liquid depends on the intermolecular forces, the structural aspects of the liquid can be inferred from the viscosity of solutions at various solute concentration and temperature.

In this paper we have attempted to report the limiting apparent molar volume (ϕ_v^0), experimental slopes (S_v^*) and viscosity B - coefficients for phosphomolybdic acid in aqueous catechol solution at 298.15, 308.15 and 318.15K. Phosphomolybdic acid is widely used to stain connective tissues by dyes. It has been found that phosphomolybdic acid forms salts with connective tissues containing basic groups and hence the polyvalent phosphomolybdic acid appears to form a bridge between the basic group of the substrate and the basic group of the dye. In other words, addition of phosphomolybdic acid to connective tissues changes its acidophilia to basophilia. Phosphomolybdic acid not only yields an intense staining of connective tissue fibers by dyes with basic groups but also reduces the staining of cytoplasm, thus producing a specific staining of connective tissue fiber ⁷.

11.2. Experimental Section

11.2.1. Chemicals

Commercial sample of catechol was purified by repeated crystallization from mixture of chloroform-methanol. The sample was dissolved in chloroform in hot condition, filtered and to the filtrate dried and distilled methanol was added drop wise. Fine plate like crystal separated and was recovered by rapid filtration and ready for use. Phosphomolybdic acid of analytical grade was purchased from Thomas Baker and was used without further purification. Doubly distilled, degassed and deionised water with a specific conductance of $1 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ was used for all measurements. Experimental values of viscosity (η), density (ρ) and pH are listed in Table 1.

11.2.2. Apparatus and procedure

Densities (ρ) were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of about 25 cm^3 and an internal diameter of about 0.1 cm. the measurements were done in a thermostat bath controlled to $\pm 0.01 \text{ K}$. the viscosity (η) was measured by means of suspended Ubbelohde type viscometer, calibrated at 298.15 K with triply distilled water and purified methanol using density and viscosity values from literature. The flow times were accurate to $\pm 0.1 \text{ s}$, and the uncertainty in the viscosity measurements was $\pm 2 \times 10^{-4} \text{ m} \cdot \text{Pas}$. The mixtures were prepared by mixing known volume of pure liquids in airtight-stopper bottles and each solution thus prepared was distributed into three recipients to perform all the measurements in triplicate, with the aim of determining possible dispersion of the results obtained. Adequate precautions were taken to minimize evaporation loses during the actual measurements. The reproducibility in mole fractions was within ± 0.0002 units. The mass measurements were done on a Mettler AG-285 electronic balance with a precision of $\pm 0.01 \text{ mg}$. The precision of density measurements was $\pm 3 \times 10^{-4} \text{ g cm}^{-3}$. Viscosity of the solution, η , is given by the following equation:

$$\eta = (Kt - L/t)\rho \quad (1)$$

where K and L are the viscometer constants and t and ρ are the efflux time of flow in seconds and the density of the experimental liquid, respectively. Details of the methods and techniques of density and viscosity measurements have been described elsewhere⁸⁻¹¹. The electrolyte solutions studied here were prepared by mass and the conversion of molality in molarity was accomplished³ using experimental density values. The experimental values of concentrations(c), densities (ρ), viscosities (η), and derived parameters at various temperatures are reported in Table 2.

11.3. Results and Discussion

The apparent molar volumes ϕ_v were determined from the solution densities using the following equation:

$$\phi_v = M/\rho_0 - 1000(\rho - \rho_0)/c\rho_0 \quad (2)$$

where M is the molar mass of the solute, c is the molarity of the solution; ρ_0 and ρ are the densities of the solvent and the solution respectively. The limiting apparent molar volumes

ϕ_v^0 was calculated using a least square treatment to the plots of ϕ_v versus \sqrt{c} using the following Masson equation¹².

$$\phi_v = \phi_v^0 + S_v^* \sqrt{c} \quad (3)$$

where ϕ_v^0 is the partial molar volume at infinite dilution and S_v^* the experimental slope. The plots of ϕ_v against square root of molar concentration \sqrt{c} were found to be linear with negative slopes. Values of ϕ_v^0 and S_v^* are reported in Table 3.

As the systems under study are characterized by hydrogen bonding, the ion-solvent and ion-ion interactions can be interpreted in terms of structural changes which arise due to hydrogen bonding between various components of the solvent

and solution systems. ϕ_V^0 can be used to interpret ion-solvent interactions. Table 3 reveals that ϕ_V^0 values are positive and increases with rise in temperature and decreases with increase in the amount of catechol in the solvent mixture. This indicates the presence of strong ion-solvent interactions and these interactions are strengthened with rise in temperature and weakened with an increase in the amount of catechol in the solvent mixture under study, suggesting larger electrostriction at higher temperature and in lower amount of catechol in the mixture. Similar results were obtained for some 1:1 electrolytes in aqueous DMF ¹³ and aqueous THF ¹⁴.

It is evident from Table 3 that the S_V^* values are negative at all temperatures for aqueous mixtures of catechol. Furthermore S_V^* values decreases with the increase of experimental temperature which may be attributed to more violent thermal agitation at higher temperatures, resulting in diminishing the force of ion-ion interactions (ionic-dissociation) ¹⁵. A quantitative comparison of the magnitude of values shows that ϕ_V^0 values are much greater in magnitude than those of S_V^* for all the solutions. This suggests that ion-solvent interactions dominate over ion-ion interactions in all the solutions and at all experimental temperatures.

The variation of ϕ_V^0 with temperature of phosphomolybdic acid in solvent mixture follows the polynomial,

$$\phi_V^0 = a_0 + a_1T + a_2T^2 \tag{4}$$

over the temperature range under study where T is the temperature in K.

Values of coefficients of the above equation for phosphomolybdic acid in aqueous catechol mixtures are reported in Table 4.

The apparent molar expansibilities ϕ_E^0 can be obtained by the following equation:

$$\phi_E^0 = \left(\delta\phi_V^0/\delta T\right)_P = a_1 + 2a_2T \tag{5}$$

The values ϕ_E^0 of for different solutions of the studied electrolytes at 298.15, 308.15 and 318.15 K are reported in Table 5. Table 5 reveals that ϕ_E^0 value increases as temperature increases up to 0.05 mol·dm⁻³ of catechol mixtures but thereafter ϕ_E^0 value decreases slightly with increasing temperature. This fact may be attributed to gradual disappearance of caging or packing effect ^{15,16} in the ternary solutions. During the past few years it has been emphasized by a number of workers that S_V^* is not the sole criterion for determining the structure-making or breaking tendency of any solute. According to Helper ¹⁷ the sign of $(\delta\phi_E^0/\delta T)_P$ is a better criterion in characterizing the long-range structure-making and breaking ability of the solutes in solution. The general thermodynamic expression used is as follows

$$(\delta\phi_E^0/\delta T)_P = (\delta^2\phi_V^0/\delta T^2)_P = 2a_2 \quad (6)$$

If the sign of $(\delta\phi_E^0/\delta T)_P$ is positive or small negative ¹⁸ the solute is a structure maker otherwise it is a structure breaker. As is evident from Table 5, phosphomolybdic acid predominately acts as a structure maker and its structure making ability decreases to some extent as the molarity of catechol increases in the solvent mixture. A similar result was observed in the study of nicotinamide in aqueous tetrabutylammonium bromide solution ¹⁹. The small negative values of $(\delta\phi_E^0/\delta T)_P$ at 0.1 and 0.15 mol·dm⁻³ aqueous catechol solution are probably due to higher structure promoting ability of catechol than phosphomolybdic acid with comparatively higher ϕ_V^0 value in aqueous solution ²⁰ originating from hydrophobic hydration with greater degree of hydrogen bonding than the bulk water ²¹.

Partial molar volume $\Delta\phi_V^0$ of transfer from water to different aqueous catechol solution has been determined using the following relation ^{22, 23}

$$\Delta\phi_V^0 = \phi_V^0[\text{Aqueous Catechol solution}] - \phi_V^0[\text{Water}] \quad (7)$$

The ϕ_V^0 value is independent from solute-solute interaction and provides information regarding solute and co-solute interaction ²². Table 3 shows that the values of ϕ_V^0 is positive at all experimental temperatures and increases with the concentration of catechol in the ternary mixture. The concentration dependence of the thermodynamic properties of the solute in aqueous solution can be explained in terms of overlap of hydration co-sphere. According to the co-sphere model as developed by Friedman and Krishnan ²⁴, the effect of the overlap of hydration co-sphere is destructive. The overlap of hydration co-spheres of two ionic species results in an increase in volume but that of hydration co-sphere of hydrophobic-hydrophobic group and ion- hydrophobic group results in a net volume decrease. The positive value of $\Delta\phi_V^0$ indicate that hydrophobic- hydrophobic and ion-hydrophobic group interaction are predominant and the overall effect of the hydration co-sphere of phosphomolybdic acid and catechol reduce the effect of electrostriction of water by phosphomolybdic acid molecule and these effect increases with the molarity of catechol in the ternary mixture as shown in the Fig. 1($\Delta\phi_V^0$ vs. molarity of catechol in solution). In addition, standard partial molar volume of the solute has been explained by a simple model ^{25,26}.

$$\phi_V^0 = \phi_{VW} + \phi_{Void} - \phi_S \quad (8)$$

Where ϕ_{VW} is the vander wall volume, ϕ_{Void} is the volume associated with void or empty space and ϕ_S the shrinkage volume due to electrostriction. Considering the ϕ_{VW} and ϕ_{Void} have the same magnitude in water and in aqueous catechol solution for the same solute ²⁷. The increase in ϕ_V^0 values and the concomitant positive $\Delta\phi_V^0$ can be attributed to the decrease in shrinkage volume of water by phosphomolybdic acid in presence of catechol. This fact suggests that catechol has a dehydrating effect on the hydrated phosphomolybdic acid.

The viscosity data of aqueous and aqueous catechol solution have been analyzed using Jones-Dole ²⁸ equation:

$$(\eta/\eta_0 - 1)/\sqrt{c} = (\eta_r - 1)/\sqrt{c} = A + B\sqrt{c} \quad (9)$$

Where η_0 and η are the viscosities of the solvent/solvent mixtures and solution respectively. A and B are the constants estimated by a least-squares method and are reported in Table 6. From the Table it is evident that the values of the A coefficient are either negative or very small positive for all the solutions under investigation at all experimental temperatures. These results indicate the presence of very weak ion-ion interactions and these interactions further decrease with the rise of experimental temperatures and increase with an increase of catechol in the mixture.

The effects of ion-solvent interactions on the solution viscosity can be inferred from the B -coefficient^{29,30}. The viscosity B -coefficient is a valuable tool to provide information concerning the solvation of the solutes and their effects on the structure of the solvent. From Table 6 it is evident that the values of the B -coefficient of phosphomolybdic acid in the studied solvent systems are positive, thereby suggesting the presence of strong ion - solvent interactions, and these types of interactions are strengthened with a rise in temperature and weakened with an increase of catechol in the mixture. These conclusions are in excellent agreement with those drawn from ϕ_v^0 values discussed earlier.

Viscosity B -coefficient of transfer (ΔB) from water to different aqueous catechol solutions have been determined using the relation^{22,23}

$$\Delta B = B [\text{Aqueous Catechol solution}] - B [\text{Water}] \quad (10)$$

The ΔB values as shown in Table 7 and depicted graphically in Fig. 2 (ΔB vs. molarity of catechol in solution) as a function of molarity of catechol in solution at the experimental temperature supports the result obtained from $\Delta\phi_v^0$ as discussed above.

The viscosity data have also been analyzed on the basis of transition state theory of relative viscosity of solutes as suggested by Feakings. et. al³¹ using the following equation

$$\Delta\mu_2^{0\ddagger} = \Delta\mu_1^{0\ddagger} + RT(1000B + \phi_{v,2}^0 - \phi_{v,1}^0) / \phi_{v,1}^0 \quad (11)$$

where $\phi_{v,1}^0$ and $\phi_{v,2}^0$ are the partial molar volumes of the solvent and the solute respectively. The contribution per mole of the solute to the free energy of activation of viscous flow $\Delta\mu_2^{0\ddagger}$ of the solutions was determined from the above relation and are listed in Table 8. The free energy of activation of viscous flow of the pure solvent $\Delta\mu_1^{0\ddagger}$ is given by the relation:

$$\Delta\mu_1^{0\ddagger} = \Delta G_1^{0\ddagger} = RT \ln(\eta_0 \phi_{v,1}^0 / hN_A) \quad (12)$$

Where N is the Avogadro's number and the other symbols have their usual significance. The values of $\Delta\mu_2^{0\ddagger}$ and $\Delta\mu_1^{0\ddagger}$ are reported in Table 8. From Table 8 it is evident that $\Delta\mu_1^{0\ddagger}$ is practically constant at all the solvent composition and temperature, implying that $\Delta\mu_2^{0\ddagger}$ is mainly dependent on the viscosity *B*-coefficients and $(\phi_{v,2}^0 - \phi_{v,1}^0)$ terms. Also $\Delta\mu_2^{0\ddagger}$ values were found to be positive at all experimental temperatures and this suggests that the process of viscous flow becomes difficult as the temperature and molarity of catechol in solution increases. Hence the formation of transition becomes less favorable ³¹. According to Feakings.et.al, $\Delta\mu_2^{0\ddagger} > \Delta\mu_1^{0\ddagger}$ for electrolytes having positive *B*-coefficients and indicates a stronger ion-solvent interactions, thereby suggesting that the formation of transition state is accompanied by the rupture and distortion of the intermolecular forces in solvent structure ³². The greater values of $\Delta\mu_2^{0\ddagger}$ supports the increased structure making tendency of the solute as discussed earlier. The entropy of activation for solutions has been calculated using the following relation ³¹.

$$\Delta S_2^{0\ddagger} = -d(\Delta\mu_2^{0\ddagger})/dT \quad (13)$$

Where $\Delta S_2^{0\ddagger}$ has been determined from the negative slope of the plots of $\Delta\mu_2^{0\ddagger}$ against T by using a least square treatment.

The activation enthalpy $\Delta H_2^{0\ddagger}$ has been calculated using the relation ³¹:

$$\Delta H_2^{0\ddagger} = \Delta\mu_2^{0\ddagger} + T\Delta S_2^{0\ddagger} \quad (14)$$

The value of $\Delta S_2^{0\ddagger}$ and $\Delta H_2^{0\ddagger}$ are listed in Table 8 and they are found to be negative for all the solutions and at all experimental temperatures suggesting that the transition state is associated with bond formation and increase in order. Although a detailed mechanism for this cannot be easily advanced, it may be suggested that the slip-plane is in the disordered state ^{31,33}.

11.4. Conclusion

The values of apparent molar volume ϕ_V^0 and viscosity B - coefficients for phosphomolybdic acid indicate the presence of strong solute-solvent interactions and these interactions are further strengthened at higher temperature and higher molarity of catechol in the ternary solutions. Also phosphomolybdic acid acts as a water-structure promoter due to hydrophobic hydration in the presence of catechol and catechol has a dehydration effect on the hydrated phosphomolybdic acid.

References

- [1] J.M. Mc Dowali, C.A. Vincent, *J. Chem. Soc. Faraday Trans.*, 1 (1974) 1862.
- [2] M.R.J. Deck, K.J. Bird, A.J. Parker, *Aust. J. Chem.*, 28 (1975) 955.
- [3] M.N. Roy, B. Sinha, R. Dey, A. Sinha, *Int. J. Thermophys.*, 26 (2005) 1549.
- [4] R.H. Stokes, R. Mills, *Int. Encyclopedia of Physical Chemistry and Chemical Physics*, Pergamon Press, London (1965).
- [5] P.S. Nikam, H. Mehdi, *J. Chem. Eng. Data*, 33 (1988) 165.
- [6] D. Nandi, M.N. Roy, D.K. Hazra, *J. Ind.Chem.Soc.*, 70(1993) 305.
- [7] H. Puchtler, H. Isler, Department of Anatomy, Mc Gill University, Montreal, Canada, (1958).
- [8] M.N. Roy, A. Sinha, B. Sinha, *J. Sol. Chem.*, 34 (2005) 1311.
- [9] M.N. Roy, B. Sinha, V.K. Dakua, *J. Chem. Eng. Data*, 51 (2006) 590.
- [10] M.N. Roy, A. Sinha, *Fluid Phase Equilib.*, 243 (2006) 133.
- [11] M.N. Roy, M. Das, *Russian. J. Phys.Chem.*, 80 (2006) S163.
- [12] D.O. Masson, *Phil.Mag.*, 8 (1929) 218.
- [13] E. Garland-Paneda, C. Yanes, J.J. Calventa, *J. Chem, Soc. Faraday Trans.*, 94 (1994) 573.
- [14] M.N. Roy, A. Jha, R. Dey, *J. Chem. Eng. Data*, 46 (2001) 1247.
- [15] F.J. Millero, *Structure and transport Process in Water and aqueous solutions*, Wiley, New York (1972).
- [16] M.L. Parmar, D.S. Banyal, *Ind. J. Chem.*, 44A (2005) 1582.
- [17] L.G. Hepler, *Can. J. Chem.*, 47 (1969) 4617.
- [18] B.K. Sarkar, B. Sinha, M.N. Roy, *Russian, J. Phys.Chem.*, 82 (2008) 1.
- [19] B. Sinha, B.K. Sarkar, M.N. Roy, *J. Chem. Thermodyn.*, 40 (2008) 394.
- [20] L.H. Blanco, E.F. Vargas, *J. Sol. Chem.*, 35 (2006) 21.
- [21] W.Y. Wen, *Water and Aqueous Solution*, Willey-Intersciences, New York (1972).
- [22] K. Belibagli, E. Agranci, *J. Solution. Chem.*, 19 (1990) 867.
- [23] C. Zhao, P. Ma, J. Li, *J. Chem. Thermodyn.*, 37 (2005) 37.
- [24] H.L. Friedman, C.V. Krishnan, F. Franks, *Water A Comprehensive Treatise*, Plenum Press, New York (1973).
- [25] R.K. Wadi, P. Ramasami, *J. Chem. Soc. Faraday Trans.*, 93 (1997) 243.

- [26] R. Bhat, J.C. Ahliwalia, *J. Phys.Chem.*, 89 (1985) 1099.
- [27] A.K. Mishra, J.C. Ahliwalia, *J. Chem. Soc. Faraday Trans*, 77 (1981) 1469.
- [28] G. Jones, M. Dole, *J. Am. Chem. Soc.*, 51 (1929) 2950.
- [29] F.J. Millero, *Chem. Rev.*, 71 (1971) 147.
- [30] F.J. Millero, A. Losurdo, C. Shin, *J. Phys. Chem.*, 82 (1978) 784.
- [31] D. Feakins, D.J. Freemantle, K.G. Lawrence, *J. Chem, Soc. Faraday Trans.*, 170 (1974) 795.
- [32] B. Samantaray, S. Mishra, U.N. Dash, *J. Teach Res Chem.*, 11(2005) 87.
- [33] M. Prasad, M. Singh, *J. Ind. Chem. Soc.*, 83 (2000) 803.

Table 1

 Density (ρ) and viscosity (η) of aqueous catechol mixtures at different temperatures.

Temperature (K)	$\rho \cdot 10^{-3}$ /kg · m ⁻³		η /mPa · s		p^H	
	Exp	Lit	Exp	Lit	Exp	Lit
0.05(M)						
298.15	0.99650	-	0.9003	-	6.16	-
308.15	0.99371	-	0.7350	-	5.31	-
318.15	0.99222	-	0.6135	-		-
0.1(M)						
298.15	0.99797	-	0.9132	-	4.20	-
308.15	0.99509	-	0.7475	-	4.16	-
318.15	0.99303	-	0.6375	-	4.13	-
0.15(M)						
298.15	0.99910	-	0.9227	-	3.97	-
308.15	0.99621	-	0.7602	-	3.89	-
318.15	0.99429	-	0.6528	-	3.82	-

Table 2

Concentration (c), density (ρ), viscosity (η), apparent molar volume (ϕ_v), $\frac{(\eta_r - 1)}{\sqrt{c}}$ and pH of phosphomolybdic acid in different aqueous catechol mixtures at different temperatures.

c /mol · dm ⁻³	$\rho \cdot 10^{-3}$ /kg · m ⁻³	η / mPa · s	$\phi_v \cdot 10^6$ /m ³ · mol ⁻¹	$\frac{(\eta_r - 1)}{\sqrt{c}}$	pH
0.00(M)					
298.15 K					
0.0025	1.0003	0.8970	963.47	0.0754	2.56
0.0050	1.0042	0.9013	807.35	0.1213	2.29
0.0074	1.0085	0.9059	709.80	0.1585	2.13
0.0099	1.0125	0.9099	693.59	0.1829	1.99
0.0124	1.0169	0.9146	649.65	0.2107	1.91
0.0154	1.0223	0.9205	593.04	0.2432	1.83
308.15 K					
0.0025	0.9972	0.7234	980.42	0.0260	2.50
0.0049	1.0008	0.7275	880.58	0.0980	2.20
0.0074	1.0048	0.7318	803.29	0.1500	2.02
0.0098	1.0091	0.7365	725.12	0.1961	1.89
0.0123	1.0135	0.7404	677.66	0.2239	1.80
0.0151	1.0189	0.7454	617.43	0.2571	1.72
318.15K					
0.0024	0.9949	0.6042	1117.80	0.2110	2.40
0.0049	0.9989	0.6170	874.40	0.4530	2.08
0.0073	1.0032	0.6280	745.77	0.5860	1.90
0.0098	1.0072	0.6378	717.08	0.6720	1.79
0.0122	1.0114	0.6469	678.22	0.7400	1.69
0.0151	1.0169	0.6583	614.98	0.8200	1.59
0.05(M)					
298.15 K					
0.0024	1.0007	0.9071	504.87	0.0860	2.73
0.0048	1.0053	0.9116	431.73	0.1330	2.36
0.0076	1.0107	0.9162	391.32	0.1637	2.14
0.0101	1.0156	0.9190	365.77	0.1727	2.03
0.0125	1.0205	0.9229	339.99	0.1940	1.92
0.0149	1.0252	0.9270	329.77	0.2145	1.83
308.15 K					

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0.0024	0.9978	0.7396	530.28	0.1280	2.66
0.0048	1.0023	0.7458	472.46	0.2130	2.29
0.0076	1.0075	0.7516	434.25	0.2600	2.08
0.0101	1.0123	0.7569	412.49	0.2970	1.98
0.0125	1.0170	0.7604	387.12	0.3100	1.85
0.0148	1.0217	0.7663	373.60	0.3492	1.77
318.15 K					
0.0024	0.9962	0.6217	569.2613	0.2750	2.58
0.0048	1.0004	0.6307	518.5812	0.4060	2.22
0.0076	1.0055	0.6421	484.1216	0.5364	1.99
0.0102	1.0094	0.6514	458.6212	0.6171	1.91
0.0126	1.0132	0.6583	424.2826	0.6560	1.83
0.0150	1.0174	0.6657	411.1519	0.7000	1.73
0.1(M)					
298.15K					
0.0024	1.0022	0.9199	510.13	0.1490	2.53
0.0048	1.0065	0.9254	491.94	0.1930	2.26
0.0076	1.0116	0.9306	471.79	0.2180	2.09
0.0101	1.0162	0.9343	456.38	0.2300	1.99
0.0125	1.0207	0.9375	440.59	0.2380	1.91
0.0149	1.0253	0.9411	423.41	0.2500	1.85
308.15 K					
0.0024	0.9992	0.7524	562.06	0.1340	2.58
0.0048	1.0034	0.7577	526.57	0.1970	2.24
0.0076	1.0084	0.7634	501.16	0.2440	2.04
0.0101	1.0130	0.7682	487.94	0.2762	1.94
0.0125	1.0173	0.7716	476.84	0.2881	1.83
0.0149	1.0219	0.7752	460.99	0.3040	1.75
318.15 K					
0.0024	0.9970	0.6441	600.01	0.2020	2.42
0.0048	1.0011	0.6518	572.64	0.3230	2.14
0.0076	1.0060	0.6604	551.50	0.4120	1.94
0.0101	1.0104	0.6662	533.72	0.4480	1.85
0.0125	1.0148	0.6731	514.62	0.5000	1.75
0.0150	1.0192	0.6806	498.54	0.5540	1.70
0.15(M)					
298.15K					
0.0024	1.0034	0.9309	480.50	0.1820	2.52
0.0050	1.0081	0.9354	462.59	0.1940	2.25
0.0076	1.0128	0.9400	458.51	0.2150	2.09
0.0102	1.0174	0.9434	445.89	0.2230	1.97
0.0125	1.0217	0.9474	439.35	0.2402	1.88

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0.0151	1.0265	0.9512	428.72	0.2520	1.81
308.15 K					
0.0024	0.0024	0.0024	0.0024	0.0024	0.0024
0.0050	0.0050	0.0050	0.0050	0.0050	0.0050
0.0076	0.0076	0.0076	0.0076	0.0076	0.0076
0.0102	0.0102	0.0102	0.0102	0.0102	0.0102
0.0125	0.0125	0.0125	0.0125	0.0125	0.0125
0.0151	0.0151	0.0151	0.0151	0.0151	0.0151
318.15 K					
0.0024	0.0024	0.0024	0.0024	0.0024	0.0024
0.0050	0.0050	0.0050	0.0050	0.0050	0.0050
0.0076	0.0076	0.0076	0.0076	0.0076	0.0076
0.0102	0.0102	0.0102	0.0102	0.0102	0.0102
0.0125	0.0125	0.0125	0.0125	0.0125	0.0125
0.0151	0.0151	0.0151	0.0151	0.0151	0.0151

Table 3

 Limiting apparent molar volumes (ϕ_V^0) and experimental slopes (S_V^*) for phosphomolybdic acid at different temperatures.

Aqueous catechol solution, mol dm ⁻³	$\phi_V^0 \cdot 10^6 / \text{m}^3 \cdot \text{mol}^{-1}$			$S_V^* \times 10^6 / \text{m}^3 \text{mol}^{-3/2} \text{dm}^{3/2}$		
	298.15K	308.15K	318.15K	298.15K	308.15K	318.15K
0.00	1163.5	1227.3	1368.4	-4757.8	-4980.3	-6440.7
0.05	607.3	626.2	673.7	-2372.1	-2128.5	-2185.7
0.10	571.4	622.6	668.4	-1174.5	-1335.1	-1371.7
0.15	513.4	609.9	639.5	-674.1	-697.1	-1000.7

Table 4

Values of the coefficients of equation (4) for phosphomolybdic acid in different aqueous catechol mixtures.

Aqueous catechol solution, mol dm ⁻³	$a_0 \cdot 10^6 / \text{m}^3 \cdot \text{mol}^{-1}$	$a_1 \cdot 10^6 / \text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$a_2 \cdot 10^6 / \text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-2}$
0.00	34772.46	-227.96	0.3865
0.05	13182.24	-84.81	0.1430
0.10	-3389.25	21.18	-0.0265
0.15	-33143.04	212.76	-0.3350

Table 5

Limiting partial molar expansibilities (ϕ_E^0) for phosphomolybdic acid in different aqueous catechol mixtures at different temperatures.

Aqueous catechol solution, mol dm ⁻³	$\phi_E^0 \cdot 10^6 / \text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$			$\left(\frac{\delta \phi_E^0}{\delta T} \right)_p \cdot 10^6$ / $\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-2}$
	298.15K	308.15K	318.15K	
0.00	2.510	10.240	17.97	0.773
0.05	0.459	3.319	6.179	0.286
0.10	5.388	4.853	4.323	-0.053
0.15	13.004	6.304	0.396	-0.670

Table 6

Values of *A* and *B* coefficients for phosphomolybdic acid in different aqueous catechol mixtures at different temperatures

Aqueous catechol solution, mol dm ⁻³	<i>A</i> / m ^{3/2} · mol ^{-1/2}			<i>B</i> / m ³ · mol ⁻¹		
	298.15K	308.15K	318.15K	298.15K	308.15K	318.15K
0.00	-0.0363	-0.1251	-0.1438	2.2454	3.1624	8.0839
0.05	0.011	0.0010	-0.0025	1.663	2.8785	5.9650
0.10	0.0941	0.0307	0.0010	1.3220	2.3322	4.5261
0.15	0.1301	0.0355	0.0048	0.9717	1.4666	1.9682

Table 7

Partial molar volumes (ϕ_V^0) and viscosity B -coefficients transfer from water to different aqueous catechol solutions for phosphomolybdic acid at different temperatures.

Aqueous catechol solution, mol dm ⁻³	$\phi_V^0 \cdot 10^6$ /m ³ · mol ⁻¹	$\Delta\phi_V^0 \cdot 10^6$ /m ³ · mol ⁻¹	B /m ³ · mol ⁻¹	ΔB /m ³ · mol ⁻¹
298.15K				
0.00	1163.5	0.00	2.2454	0.00
0.05	607.33	556.17	1.663	0.5824
0.10	571.38	592.12	1.3220	0.9234
0.15	513.4	650.1	0.9717	1.2737
308.15K				
0.00	1227.3	0.00	3.1624	0.00
0.05	626.22	601.08	2.8785	0.2839
0.10	622.56	604.74	2.3322	0.8302
0.15	609.94	617.36	1.4666	1.6958
318.15K				
0.00	1368.4	0.00	8.0839	0.00
0.05	673.7	694.70	5.956	2.1279
0.10	668.44	699.96	4.5261	3.5578
0.15	639.48	728.92	1.9682	6.1157

Table 8

 Values of $(\phi_{V,2}^0 - \phi_{V,1}^0) \cdot 10^6 / \text{m}^3 \cdot \text{mol}^{-1}$, $\Delta\mu_1^{0\#}$, $\Delta\mu_2^{0\#}$, $T\Delta S_2^{0\#}$ and $\Delta H_2^{0\#}$ for phosphomolybdic acid in different aqueous catechol mixtures at different temperatures.

Parameter	308.15K		
	298.15K		318.15K
	0.00, mol dm ⁻³		
$(\phi_{V,2}^0 - \phi_{V,1}^0) \cdot 10^6 / \text{m}^3 \cdot \text{mol}^{-1}$	1145.43	1209.17	1350.24
$\Delta\mu_1^{0\#} / \text{kJ} \cdot \text{mol}^{-1}$	60.82	62.86	64.90
$\Delta\mu_2^{0\#} / \text{kJ} \cdot \text{mol}^{-1}$	465.134	617.891	1373.86
$T\Delta S_2^{0\#} / \text{kJ} \cdot \text{mol}^{-1}$	-13546.71	-14001.1	-14455.5
$\Delta H_2^{0\#} / \text{kJ} \cdot \text{mol}^{-1}$	-13081.609	-13383.21	-13081.60
	0.05, mol dm ⁻³		
$(\phi_{V,2}^0 - \phi_{V,1}^0) \cdot 10^6 / \text{m}^3 \cdot \text{mol}^{-1}$	589.10	607.89	655.32
$\Delta\mu_1^{0\#} / \text{kJ} \cdot \text{mol}^{-1}$	60.84	62.89	64.93
$\Delta\mu_2^{0\#} / \text{kJ} \cdot \text{mol}^{-1}$	222.02	317.90	349.47
$T\Delta S_2^{0\#} / \text{kJ} \cdot \text{mol}^{-1}$	-1899.99	-1963.72	-2027.44
$\Delta H_2^{0\#} / \text{kJ} \cdot \text{mol}^{-1}$	-1677.97	-1645.81	-1677.97
	0.1, mol dm ⁻³		
$(\phi_{V,2}^0 - \phi_{V,1}^0) \cdot 10^6 / \text{m}^3 \cdot \text{mol}^{-1}$	553.12	604.20	650.00
$\Delta\mu_1^{0\#} / \text{kJ} \cdot \text{mol}^{-1}$	60.85	62.90	64.94
$\Delta\mu_2^{0\#} / \text{kJ} \cdot \text{mol}^{-1}$	187.13	228.51	257.89
$T\Delta S_2^{0\#} / \text{kJ} \cdot \text{mol}^{-1}$	-1054.85	-1090.23	-1125.61
$\Delta H_2^{0\#} / \text{kJ} \cdot \text{mol}^{-1}$	-867.72	-861.72	-867.72
	0.15, mol dm ⁻³		
$(\phi_{V,2}^0 - \phi_{V,1}^0) \cdot 10^6 / \text{m}^3 \cdot \text{mol}^{-1}$	495.10	591.54	621.00
$\Delta\mu_1^{0\#} / \text{kJ} \cdot \text{mol}^{-1}$	60.86	62.90	64.96
$\Delta\mu_2^{0\#} / \text{kJ} \cdot \text{mol}^{-1}$	88.55	147.27	177.11
$T\Delta S_2^{0\#} / \text{kJ} \cdot \text{mol}^{-1}$	-1320.21	-1364.49	-1408.77
$\Delta H_2^{0\#} / \text{kJ} \cdot \text{mol}^{-1}$	-1231.66	-1217.22	-1231.66

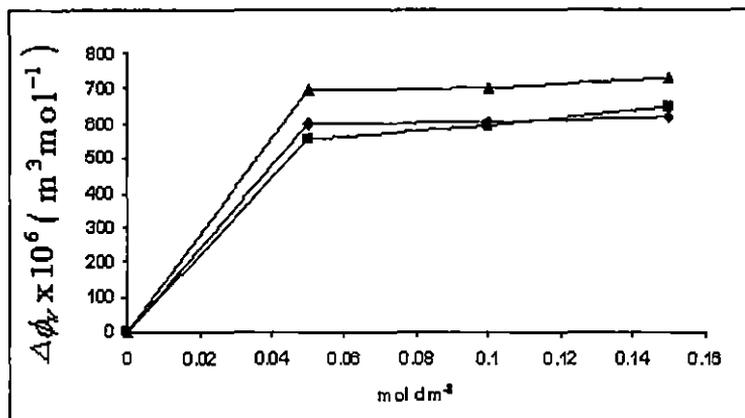


Figure 1. Plots of partial molar volume ($\Delta\phi_v^0$) against molality for the transfer from water to different aqueous catechol solution for phosphomolybdic acid at different temperatures ;T=298.15K (■); T=308.15K (◆); T=318.15K (▲).

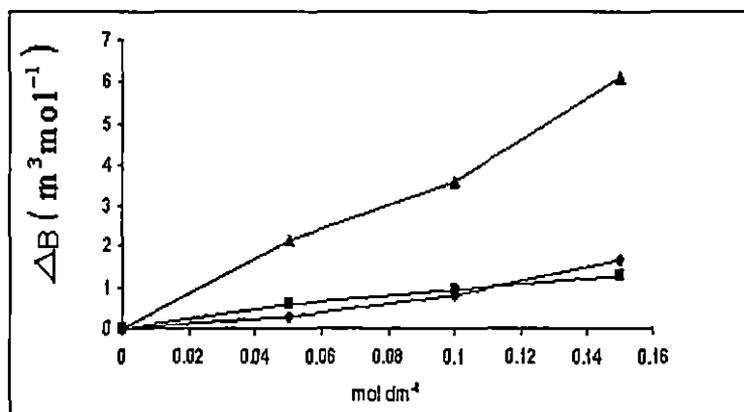


Figure 2. Plots of viscosity *B*-coefficient (ΔB) against molality for the transfer from water to different aqueous catechol solution for phosphomolybdic acid at different temperatures. T=298.15K (■); T=308.15K (◆); T=318.15K (▲).