Thermodynamic Dissociation Constants of Propionic Acid in Water and 1-Propanol Mixtures between 303.15 and 323.15 K

[1, 3]A. K. M. Atique Ullah*, [2]Mahmuda Akter and [3]Shakhawat Hossain Firoz
[1]*Chemistry Division, Atomic Energy Centre, Bangladesh Atomic Energy Commission,*
Dhaka-1000, Bangladesh.
[2]*Department of Environmental Science, Stamford University Bangladesh, Dhaka-1209, Bangladesh.*
[3]*Department of Chemistry, Bangladesh University of Engineering and Technology (BUET),*
Dhaka-1000, Bangladesh.
atique.chem@gmail.com*

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Summary: Thermodynamic dissociation constants (K_a) of propionic acid in 0, 5, 10 and 20 wt% 1-propanol-water binary mixtures have been determined between 303.15 and 323.15 K. A conductometric method has been applied to measure the molar conductance of dilute solutions of propionic acid. Fuoss-Kraus conductance equation has been applied to calculate the values of limiting molar conductance (Λ_0) and thermodynamic ionization constant (K_a). It was found that both the values of K_a and Λ_0 decreased by the increasing of amount of 1-propanol in the binary mixtures. However, K_a values were decreased and Λ_0 values were increased by increasing temperatures. The normalized Walden products of the propionic acid have been calculated. Thermodynamic quantities such as change of standard free energy (ΔG°), change of standard enthalpy (ΔH°) and change of standard entropy (ΔS°) have been calculated in case of each of the binary mixtures.

Key Words: Propionic acid, 1-Propanol, Conductance, Dielectric Constant, Walden Product.

Introduction

There have been much recent interests on the use of binary solvent mixtures for many theoretical and practical purposes such as pharmaceutical research, environmental remediation, etc [1-3]. These mixtures have also been used as solvents in the study of various physicochemical properties of electrolytes like dissociation, association, solubility and stability [4, 5]. The dissociation of weak electrolytes depends on their physical and chemical properties. It also depends on the solvent properties including polarity, dielectric constant, viscosity and factors such as temperature and pH of the solvent mixtures [6]. Dissociation constants and thermodynamic parameters for acid-base equilibria in solvents comprising binary aqueous mixtures are helpful in understanding the solvent effects on weak electrolytes.

To study the dissociation behavior, a quite number of reports on the conductometric studies of different electrolytes in both water and mixed solvent mixtures have recently been published [7-13]. From the reports it was observed that the dissociation of weak electrolytes generally decreased by the increasing of nonaqueous solvent in water and cosolvent mixtures. The thermodynamic dissociation constants of propionic acid in water between 323 and 623 K are reported [14]. The investigators found that the dissociation constants of propionic acid decreased by increasing temperatures. Bhattacharya *et al* [15] also determined the dissociation constants of propionic acid in ethanol-water media from 288 K to 308 K by an electromotive force method. They reported that the pK_a values of propionic acid at all temperatures showed an increase as the proportion of organic component in the medium was increased.

In order to gather more information about the nature of the solute interactions of weak acid with alcohol-water binary solvent mixtures, a conductometric study of dissociation of propionic acid in 0, 5, 10 and 20 wt% 1-propanol and water solvent mixtures has been undertaken in the present study. The limiting molar conductance, Λ_0 and dissociation constants, K_a of propionic acid were measured at different temperatures. Thermodynamic quantities namely change of standard free energy (ΔG°), change of standard enthalpy (ΔH°) and change of standard entropy (ΔS°) have also been calculated.

Results and Discussion

Limiting Molar Conductance and Dissociation Constant

Specific conductance of dilute solutions of propionic acid was read directly from the conductivity meter. The obtained values of the molar conductance for solutions of various concentrations of the acid are summarized in Table-1.

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[*] **To whom all correspondence should be addressed.**

Table-1: Molar conductance (Λ) for solutions of propionic acid in 1-propanol and water mixtures at various temperatures and varying concentration of cosolvent.

% solution 1-propanol	Concentration (C) ×10^4 (mole litre^{-1})	Molar conductance (Λ)				
		Temperature 303.15 K	Temperature 308.15 K	Temperature 313.15 K	Temperature 318.15 K	Temperature 323.15 K
0 wt%	3.7116	66.019	65.796	63.781	61.541	59.212
	4.8364	59.201	58.515	56.751	54.379	52.519
	5.9111	53.954	53.289	51.598	49.168	47.772
	6.9391	50.303	49.474	47.845	45.971	44.086
	7.9234	47.033	46.571	45.056	43.163	41.649
	8.8667	44.461	44.210	42.631	40.827	39.474
	9.7714	42.353	41.942	40.731	39.075	37.559
5 wt%	3.7116	52.982	51.383	49.855	48.498	46.673
	4.8364	47.185	45.696	44.325	42.380	41.075
	5.9111	42.931	41.447	40.263	38.571	37.219
	6.9391	39.774	38.333	37.180	35.883	34.586
	7.9234	37.231	36.096	34.959	33.698	32.436
	8.8667	35.307	34.135	33.158	32.029	30.787
	9.7714	33.772	32.646	31.623	30.395	29.371
10 wt%	3.7116	43.731	43.465	41.495	41.239	40.378
	4.8364	38.559	38.252	36.598	35.977	35.325
	5.9111	34.947	34.611	33.324	32.748	32.135
	6.9391	32.425	32.138	30.839	30.419	30.013
	7.9234	30.515	30.108	28.902	28.497	28.018
	8.8667	28.935	28.571	27.406	27.093	26.504
	9.7714	27.545	27.427	26.135	25.789	25.278
20 wt%	3.7116	26.907	26.261	25.735	25.204	24.755
	4.8364	23.665	23.194	22.704	22.131	21.818
	5.9111	21.516	20.997	20.639	20.106	19.793
	6.9391	19.943	19.379	19.123	18.651	18.302
	7.9234	18.623	18.174	17.885	17.465	17.145
	8.8667	17.645	17.192	16.917	16.516	16.215
	9.7714	16.835	16.477	16.075	15.695	15.465

It may be mentioned here that for the determination of limiting molar conductance (Λ_0) and dissociation constant (K_a) using Fuoss-Kraus equation, an initial extrapolation of Λ vs. √C was required in order to obtain a tentative value of the limiting conductance (Λ_0') which is not possible in case of weak acid like propionic acid. So the Bray-Kraus [16] equation (1) was first applied to get the Λ_0' values of the acid. The least square fitting of the plot $1/\Lambda$ vs. ($\Lambda \times C$) were used for that purpose.

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_0'} + \frac{\Lambda \times C}{K_a \times \Lambda_0'^2} \quad ....(1)$$

The values of Λ_0' were used in equation (7). Then the values of limiting molar conductance, Λ_0 and dissociation constant, K_a of the acid were calculated using Fuoss-Kraus [17] equation (2).

$$\frac{F_{(z)}}{\Lambda} = \frac{1}{\Lambda_0} + \frac{\Lambda \times C \times f_{\pm}^2}{K_a \times \Lambda_0^2 \times F_{(z)}} \quad ....(2)$$

where, $F_{(z)}$ called the Fuoss function is expressed as

$$F_{(z)} = \frac{4}{3}\cos^2\left[\frac{1}{3}\left\{\cos^{-1}\left(-3^{\frac{3}{2}} \times \frac{Z}{2}\right)\right\}\right] \quad ....(3)$$

$$Z = \frac{\left(\alpha \Lambda_0' + \beta\right)}{\left(\Lambda_0'\right)^{\frac{3}{2}}} \times \sqrt{\Lambda \times C} \quad ....(4)$$

$$\log f_{\pm} = -\frac{A\sqrt{\mu}}{1+\sqrt{\mu}} \quad ....(5), \quad \sqrt{\mu} = \sqrt{\alpha' C} \quad ....(6)$$

for weak electrolytes, and $\alpha' = \frac{\Lambda}{\Lambda_0'}$ ....(7)

α, β and A are characteristic solvent properties,

where $\alpha = 0.8204 \times 10^6 / (DT)^{\frac{3}{2}}$ ....(8)

$$\beta = 82.501/\eta(DT)^{\frac{1}{2}} \quad ....(9)$$

$$A = 1.8246 \times 10^6 / (DT)^{\frac{3}{2}} \quad ....(10)$$

Here, D is the dielectric constant and η is the viscosity of the media. The extrapolated values of D and η of 1-propanol-water solvent mixtures taken from the literatures [18, 19] were used for the calculation of solvent parameters using the equations (8-10). The values of physico-chemical and characteristic solvent properties of 1-propanol and water binary mixtures are shown in Table-2 and 3 respectively.

Table-2: Physico-chemical properties of 1-propanol and water mixtures at various temperatures.

% of 1-propanol	Property	Temperature (K)				
		303.15 K	308.15 K	313.15 K	318.15 K	323.15 K
0 wt%	D	76.76	75.18	73.35	71.57	70.10
	η (mp)	8.007	7.225	6.560	5.988	5.494
5 wt%	D	71.67	70.05	68.05	66.79	65.66
	η (mp)	11.30	8.30	6.40	4.55	3.32
10 wt%	D	70.12	68.56	66.81	65.44	63.66
	η (mp)	12.70	9.84	7.80	6.20	4.90
20 wt%	D	63.33	61.88	60.24	58.96	57.23
	η (mp)	15.82	13.10	11.04	9.44	8.30

Table-3: Solvent parameters for 1-propanol and water mixtures at various temperatures.

% of 1-Propanol	Temperature (K)	Characteristic properties of 1-propanol and water mixtures		
		α	β	A
0 wt%	303.15 K	0.2311	67.5450	0.5140
	308.15 K	0.2327	75.0221	0.5175
	313.15 K	0.2356	82.9811	0.5241
	318.15 K	0.2388	91.3053	0.5310
	323.15 K	0.2406	99.7722	0.5352
5 wt%	303.15 K	0.2562	49.5317	0.5697
	308.15 K	0.2586	67.6544	0.5753
	313.15 K	0.2637	88.3057	0.5865
	318.15 K	0.2648	124.3873	0.5891
	323.15 K	0.2654	170.5959	0.5904
10 wt%	303.15 K	0.2647	44.5559	0.5887
	308.15 K	0.2672	57.6830	0.5942
	313.15 K	0.2711	73.1253	0.6029
	318.15 K	0.2731	92.2210	0.6074
	323.15 K	0.2780	117.3891	0.6184
20 wt%	303.15 K	0.3084	37.6374	0.6859
	308.15 K	0.3116	45.6070	0.6929
	313.15 K	0.3166	54.4091	0.7042
	318.15 K	0.3193	63.8106	0.7102
	323.15 K	0.3262	73.0915	0.7255

The values of K_a and Λ_0 of propionic acid in 1-propanol and water solvent mixtures at the various temperatures were calculated from the slopes and intercepts of Fuoss-Kraus equation. The least square fitting of the plot $F_{(z)}/\Lambda$ vs. $(\Lambda \times C \times f_{\pm}^{2})/F_{(z)}$ were used for that purpose. The obtained values of Λ_0 and pK_a are summarized in Table-4.

From the Table 4 it is found that the values of limiting molar conductance (Λ_0) of propionic acid were decreased with the increase in 1-propanol concentration in the binary mixtures and are graphically represented by the Fig. 1.

This lowering of the values of limiting molar conductance (Λ_0) may be resulted due to comparative increase in the viscosities of 1-propanol-water mixtures. It is also remarkable that the values of Λ_0 are increased by the increasing temperature. It would probably mean that the increase of Λ_0 may be the resultant of the effect facilitating the thermal movement of the ions.

The pK_a values of propionic acid as shown in Fig. 2 indicate an increase of pK_a with the increase in 1-propanol concentration in the solvent mixtures and also increase with the rise of temperature.

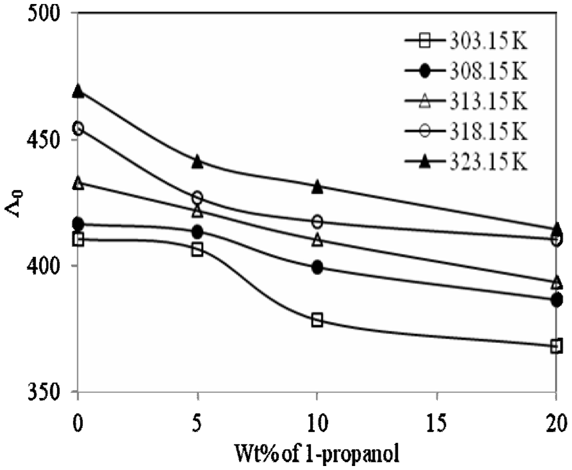

Fig. 1: Plots of Λ_0 of propionic acid versus wt% concentration of 1-propanol and water mixtures at various temperatures.

The values of pK_a of propionic acid plotted against the value of dielectric constants of the binary mixtures as shown in Fig. 3 show an approximately linear dependence on the reciprocal of the dielectric constants of the media. A similar trend in pK_a versus 1/D plots of other weak acids was reported earlier in alcohol-water binary mixtures [20]. The decrease in K_a with the increase of the alcohol concentration (as dielectric constant decreases) is due to the dominating influence of coulombic forces of attraction [21, 22].

Table-4: Λ_0 and pK_a of propionic acid in different 1-propanol and water mixtures at various temperatures.

% of 1-PrOH	Temperature (K)									
	303.15 K		308.15 K		313.15 K		318.15 K		323.15 K	
	Λ_0	pK_a	Λ_0	pK_a	Λ_0	pK_a	Λ_0	pK_a	Λ_0	pK_a
0 wt%	**410.633**	**4.913**	**416.402**	**4.959**	**433.341**	**5.027**	**454.753**	**5.109**	**469.461**	**5.171**
5 wt%	**406.669**	**5.141**	**413.486**	**5.186**	**422.135**	**5.233**	**427.119**	**5.277**	**441.794**	**5.340**
10 wt%	**378.754**	**5.262**	**399.534**	**5.317**	**410.599**	**5.379**	**417.619**	**5.411**	**431.705**	**5.453**
20 wt%	**368.378**	**5.684**	**386.723**	**5.742**	**393.702**	**5.773**	**410.493**	**5.828**	**414.524**	**5.856**

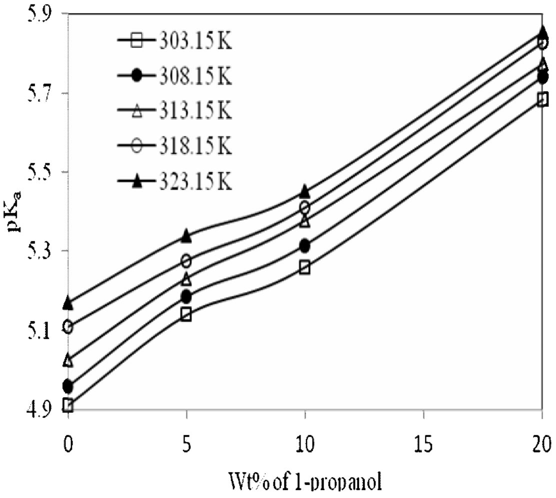

Fig. 2: Plots of pK_a of propionic acid against wt% concentraion of 1-propanol and water mixtures at various temperatures.

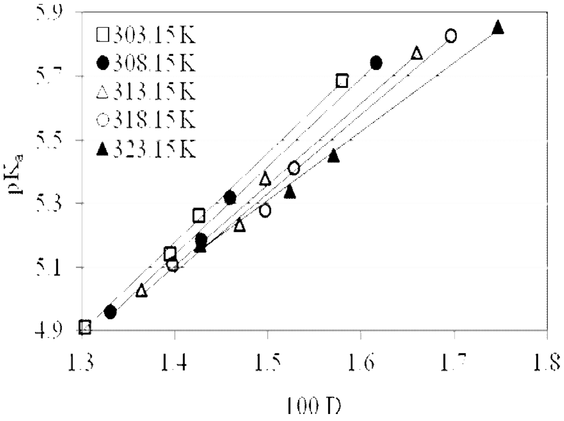

Fig. 3: Plots of pK_a of propionic acid as a function of dielectric constants (D) of 1-propanol and water mixtures at various temperatures.

Normalized Walden Product

The ratio of the value of Walden product of the acid in the solvent mixture to that in water termed as normalized Walden product, nwp ($\eta^s\Lambda_0^s/\eta^w\Lambda_0^w$) is found to be dependent on the composition of solvent for the acid studied as mentioned in the Fig. 4.

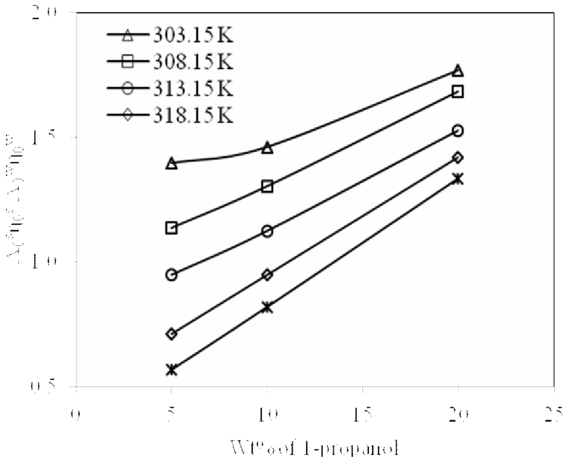

Fig. 4: Plots of Normalized Walden Product ($\Lambda_0^s\eta^s/\Lambda_0^w\eta^w$) versus wt% concentration of 1-propanol and water mixtures at various temperatures.

An increase in normalized Walden product value with the increase in 1-propanol concentration of the solvent mixture was observed within the studied composition range of the binary mixtures. A similar trend in the normalized Walden product values of weak acids like benzoic, ortho-, meta- and para-toluic acid in mixed solvents such as 1-propanol-water, ethanol-water mixtures was observed by the earlier workers [20, 23].

Thermodynamic Parameters

Thermodynamic equation, $\Delta G^0 = \Delta H^0 - T\Delta S^o = -RT\ln K_a$ can be re-rearranged to get the expression

$$-\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} = \ln K_a$$

From the plot of $\ln K_a$ vs. 1/T, ΔH° and ΔS° were obtained from the slope and the intercept respectively. The calculated values of ΔG°, ΔH° and ΔS° of the acid in different solvent mixtures at various temperatures are presented in Table-5.

Table-5: Thermodynamic parameters of propionic acid in 1-propanol and water mixtures at various temperatures

% of 1-propanol	Temperature (T)	Thermodynamic parameters		
		ΔG° (cal mole^{-1})	-ΔH° (cal mole^{-1})	-ΔS° (cal mole^{-1})
0 wt%	**303.15 K**	**6815.347**	**5942.416**	**42.029**
	308.15 K	**6992.751**		
	313.15 K	**7203.658**		
	318.15 K	**7438.059**		
	323.15 K	**7646.637**		
5 wt%	**303.15 K**	**7131.764**	**4364.191**	**37.900**
	308.15 K	**7312.847**		
	313.15 K	**7498.855**		
	318.15 K	**7682.646**		
	323.15 K	**7896.547**		
10 wt%	**303.15 K**	**7299.619**	**4261.239**	**38.162**
	308.15 K	**7497.572**		
	313.15 K	**7708.072**		
	318.15 K	**7877.733**		
	323.15 K	**8063.646**		
20 wt%	**303.15 K**	**7885.032**	**3846.782**	**38.724**
	308.15 K	**8096.689**		
	313.15 K	**8272.671**		
	318.15 K	**8484.832**		
	323.15 K	**8659.584**		

The ΔG° values were increased by the increasing of percentage composition of 1-propanol in the mixed solvent systems at all temperatures. The positive values of ΔG° explain that the acid when dissolved in these mixed solvent systems followed non-spontaneous dissolution process in forward direction hence, producing positive values of ΔG° [24-26]. The ΔH° and ΔS° values of propionic acid in the solvent mixtures were found to be negative. The entropy values of the systems having some scattering showing decrease and increase values, within percentage composition of mixed solvent systems. The mixed solvent systems decrease the ΔS° values compared to pure aqueous system. This behavior justifies that the presence of mixed solvent systems increased orderness in the molecular state of propionic acid. The negative values of ΔH° reveal the exothermic nature of propionic acid.

Experimental

Propionic acid of 99.5% purity was obtained from RDH and used as such. 1-propanol (RDH product of 99% purity) was distilled under atmospheric pressure and used for preparation of mixed solvents. Double distilled water with the specific conductance of 1.2×10^{-6} ohm^{-1}cm^{-1} at room temperature was used for the preparation of binary solvent mixtures and as an aqueous medium. Stock mixed solvents were prepared following (w/w) 1-propanol in water. A stock solution of the acid was prepared by dissolving weighed amount of the solute in a definite volume of the solvent, secondary stock solutions were prepared from this solution by dilution. During conductance measurement, different aliquots of the stock acid solution were added to a suitable volume of the solvent to prepare solutions of different concentrations. Conductance readings were carried out using a conductivity meter, Model WTW-90 (Sandberg and Schneidewind, Hamburg) with dip type cell. The accuracy of the cell was ± 1%. Thermostatic water bath having a temperature accuracy of ± 0.05 $^{\circ}$C was used for equilibrating all solutions before conductance measurement.

Conclusion

The limiting molar conductance (Λ_0) and thermodynamic dissociation constants (K_a) of propionic acid in 0, 5, 10 and 20 wt% of 1-propanol-water mixtures at temperatures between 303.15 and 323.15 K have been determined conductometrically using Fuoss-Kraus equation. It was found that the pK_a values of propionic acid increase when both temperatures and contents of 1-propanol in the solvent mixtures increase. The values of Λ_0 of the acid decrease when the contents of the alcohol in the mixture increase, whereas, Λ_0 values increase when the temperatures increase. The values of normalized Walden products increase by the increasing of the contents of the alcohol in the mixtures. The positive values of ΔG° throughout the studied range of temperature and composition of binary mixtures indicate that the dissociation of the acid in the mixtures is nonspontaneous. The higher value of ΔS° in the pure solvent than in the mixed solvent systems implies that the present of mixed solvent systems increased orderness in the molecular state of propionic acid. The negative values of ΔH° in the whole system indicate that the nature of propionic acid in 1-propanol and water mixtures is exothermic

References

1. J. T. Rubino and S. H. Yalkowsky, *Pharmaceutical Research*, **4**, 220 (1987).
2. J. T. Rubino and S. H. Yalkowsky, *Pharmaceutical Research*, **4**, 231 (1987).

3. P. T. Imhoff, S. Glyzer, J. McBride, L. Vancho, I. Okuda and T. Miller, *Environmental Science and Technology*, **29**, 1966 (1995)
4. P. A. Sonkar, P. S. Suryavanshi, S. H. Sutar and S. T. Shukla, *Journal of Chemical Pharmaceutical Research*, **4**, 1978 (2012).
5. E. A. Gomaa, *Food and Public Health*, **2**, 65 (2012).
6. A. Jouyban, *Journal of Pharmacy and Pharmaceutical Science,* **11**, 32 (2008)
7. J. I. Bhat and M. N. Manjunatha, *Indian Journal of Chemical Technology*, **17**, 462 (2010).
8. I. Tominic, R. Tomas, M. Visic and V. Sokol, *Croatica Chemica Acta*, **77**, 537 (2004).
9. M. A. Rauf, M. Ikram, U. Ehsan and A. Iqbql, *Journal of Chemical Society of Pakistan*, **20**, 275 (1998).
10. M. S. K. Niazi and M. Z. I. Khan, *Journal of Solution Chemistry*, **22**, 437 (1993).
11. M. M. Sanchez, C. Moran, C. Quintana and A. Vivo, *Journal of Solution Chemistry*, **18**, 993 (1989).
12. A. A. Ansari and M. R. Islam, *Canadian Journal of Chemistry*, **66**, 1720 (1988).
13. Y. P. Handa and G. C. Benson, *Journal of Solution Chemistry*, **10**, 291 (1981).
14. E. M. Yezdimer, J. Sedlbauer and R. H. Wood, *Chemical Geology,* **164**, 259 (2000).
15. D. C. Bhattacharya, S. K. Sarkar and A. K. Basu, *Journal of Indian Chemical Society*, **66**, 872 (1989).
16. C. A. Kraus and W. C. Bray, *Journal of American Chemical Society,* **35**, 1315 (1913).
17. R. M. Fuoss and C. A. Kraus, *Journal of American Chemical Society,* **55**, 476 (1933).
18. Y. Y. Akhadov, *Dielectric Properties of Binary Solutions*, Pergamon Press, London, p 282 (1981).
19. S. Akhtar, M. M. H. Bhuiyan, M. S. Uddin, B. Sultana, M. Nessa and M. A. Saleh, *Physics and Chemistry of Liquids*, **37**, 215 (1999).
20. M. S. K. Niazi, S. S. Shah, J. Ali and M. Z. I. Khan, *Journal of Solution Chemistry*, **19**, 623 (1990).
21. D. J. Glover, *Journal of American Chemical Society*, **87**, 5275 (1965).
22. D. W. Fong and E. Grunwald, *Journal of Physical Chemistry*, **73**, 3909 (1969).
23. M. S. K. Niazi, M. Z. I. Khan and A. Ahmes, *Bulletin of the Chemical Society of Japan*, **63**, 581 (1990).
24. A. H. Aktas and S. Yasar, *Acta Chimica Slovenia*, **51**, 273 (2004).
25. J. A.T. Trejo Gonzalez, M. P. Longinotti and H. R. Corti, *Journal of Chemical and Engineering Data*, **56**, 1397 (2011).
26. S. J. Hawkes, *Journal of Chemical Education,* **75**, 1179 (1995).

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